THE
ELECTRONIC CONCEPT ON
OF VALENCE AND THE
CONSTITUTION OF BENZENE

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WITH DIAGRAMS

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TO MY WIFE

PREFACE.

THE electronic conception of valence as developed and applied in this monograph is concerned neither with the question of the ultimate nature of chemical affinity nor with the intimately related problem of the constitution of the atom The variety of hypotheses now current, which deal with the constitution of the atom, has signally failed to furnish a uniform valence hypothesis which will enable chemists to *elucidate* chemical formulæ and reactions, or, in other words, to present more complete pictures of the relationships existing between the chemical constitution of substances and their chemical, physico-chemical and physical properties

After studying the many anomalous hypotheses on atomic structure and valence, the author has adopted the early and relatively simple suggestion of Sir J J Thomson that "if we interpret the 'bond' of the chemist as indicating a unit Faraday tube, connecting charged atoms in the molecule, the structural formulæ of the chemist can be at once translated into the electrical theory". Accordingly, the symbol—a short straight line between atoms—which indicates a "bond" in a structural formula, assumes an added significance since one end of the bond corresponds to a positive, the other to a negative charge, through the transference of an electron from the one atom to the other.

This, briefly, is *the electronic conception of positive and negative valence* which is employed herewith, solely as *a formulative hypothesis*. It is applied to the formulæ of many substances but chiefly to *the constitution of benzene.*

Methods are proposed and fully illustrated explaining how *structural formulæ* may be translated into *electronic formulæ* but only when it may be clearly demonstrated that the resultant electronic formulæ possess greater significance in interpreting and correlating chemical and physico-chemical phenomena than do our customary structural formulæ

The monograph is divided into four parts. Part I develops the electronic conception of positive and negative valence as a formulative hypothesis in chemistry Part II. relates particularly to the constitution of benzene and its derivatives, and to the problem of substitution in the benzene nucleus Part III deals primarily with physical and physico-chemical properties, notably, molecular volumes, absorption of light and fluorescence Part IV. considers the constitution of the metal-ammines and presents a bibliographical and chronological review of those articles of authors who have presented *applications* of the electronic conception of valence

Concordant with the fact that the preface is usually the last part of a book to be written, a more comprehensive preface may be found in Section A of the final chapter

In conclusion, I am deeply grateful to my colleague, Dr Earl F. Farnau, for valued suggestions, criticisms, and his reading of the manuscript, and also to Miss Eva Hauck, Secretary of the Department of Chemistry, University of Cincinnati, for the preparation of the index of names and the transcription of the manuscript.

UNIVERSITY OF CINCINNATI,
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PART I

THE ELECTRONIC CONCEPTION OF VALENCE

CHAPTER I

INTRODUCTORY.

THEORIES of valency may be divided into two general classes. J N Friend states that "to the first of these belong such theories as those of Werner and of Barlow and Pope, which postulate certain definite attractive or repellent forces, and then proceed to a discussion of the constitution of the molecule" These are designated as chemical theories of valency Theories of the second class relate to the actual causes of chemical affinity and are influenced by the particular ideas of atomic structure held by their originators Friend states that "the electronic theory of valency is a case in point, and as such is a subject for the physicist rather than the chemist"

Chemists, in general, will subscribe to this statement, because the various hypotheses on atomic structure and the fundamental nature of valence now in vogue are too diverse and too limited in their capacity either to interpret or to correlate definite chemical and physico-chemical phenomena Be this as it may, there are certain simple aspects of the electronic conception of the constitution of the atom that may be translated directly into an *electronic conception of valence* This, it will be shown, readily lends itself to the interpretation and correlation of many hitherto unexplained chemical and physico-chemical phenomena In other words, the chemist may employ the electronic conception of valence as a *formulative hypothesis* in the field of chemistry

The general purpose of this monograph is to show that the application of the electronic conception of positive and negative valences to the constituent atoms of elements and compounds leads to the development of a new type of structural chemical formula—*the electronic formula*—which is far more significant than the customary structural formula in its adaptation to the interpretation and correlation of chemical and physico-chemical phenomena

To this end, there is presented a complete revision and an extended development of the subject matter of two separate series of articles published by the author during the past twelve years. One series, which appeared in the *Zeitschrift fur physikalische Chemie* under the general title *Einige Anwendungen der Elektronischen Auffassung positiver und negativer Valenzen*, presented new hypotheses on the relationship between chemical constitution and the phenomena of light absorption and fluorescence The other series appeared concurrently in the *Journal of the American Chemical Society* under the title *Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences* In the majority of these articles an attempt was made to throw some light upon the manifold and ever recurrent problem of the *constitution of benzene* An application of the electronic conception of positive and negative valences to the constituent atoms of the benzene molecule culminated in the *electronic formula of benzene* This formula is readily adaptable to and makes possible the interpretation of many chemical and stereochemical problems presented by benzene and its derivatives

My grateful acknowledgments are due to Sir J J. Thomson whose earlier ideas on valency, as presented in his volume *Electricity and Matter* and subsequently elaborated in his *Corpuscular Theory of Matter*, directly led me to conceive, propose, and to apply the terms *electromer* and *electronic tautomerism* as fundamental concepts in the development of his electronic conception of valence The *electromer* is a new type of isomer—the electronic isomer *Electronic tautomerism* is a new type of tautomerism involving *electromers in dynamic equilibrium.*

The proposal of these new conceptions naturally involves the question of the actual existence of electromers. A few chemists have not, and others may not, be inclined to countenance the electronic conception of valence, electronic isomerism, and tautomerism chiefly upon the grounds that the independent existence of electromers has not as yet been fully established. In view of this attitude, it should be clearly understood that the question of the actual existence of electromers is a secondary matter which does not in any sense invalidate the use and significance of the electronic conception of valence as a *formula-*

tive hypothesis in chemistry The conceptions of electronic isomerism and electronic tautomerism are necessary adjuncts of the electronic conception of valence Furthermore, these conceptions are necessarily demanded by and, therefore, warranted in the interpretation and correlation of many chemical phenomena A statement of historic and prophetic interest, made by Kekulé in 1867, illustrates the principle at issue —

"The question whether atoms exist or not has but little significance from a chemical point of view its discussion belongs rather to metaphysics In chemistry we have only to decide whether the assumption of atoms is an hypothesis adapted to the explanation of chemical phenomena More especially have we to consider the question whether a further development of the atomic hypothesis promises to advance our knowledge of the mechanism of chemical phenomena.

"I have no hesitation in saying that, from a philosophical point of view, I do not believe in the actual existence of atoms, taking the word in its literal signification of indivisible particles of matter—I rather expect that we shall some day find for what we now call atoms a mathematico-mechanical explanation, which will render an account of atomic weight, of atomicity, and of numerous properties of the so-called atoms As a chemist, however, I regard the assumption of atoms, not only as advisable, but as absolutely necessary in chemistry I will even go further, and declare my belief that *chemical atoms exist*, provided the term be understood to denote those particles of matter which undergo no further division in chemical metamorphoses Should the progress of science lead to a theory of the constitution of chemical atoms—important as such a knowledge might be for the general philosophy of matter—it would make but little alteration in chemistry itself The chemical atoms will always remain the chemical unit; and for the specially chemical considerations we may always start from the constitution of atoms, and avail ourselves of the simplified expression thus obtained, that is to say, of the atomic hypothesis. We may, in fact, adopt the view of Dumas and of Faraday, that *whether matter be atomic or not, thus much is certain, that granting it to be atomic, it would appear as it now does*"

Apropos of the above quotation, let it be recalled that Kekulé's efforts to develop an understanding of the mechanism of chemical reactions are embodied to-day in the *structure theory*, the recognized foundation of the extensive achievements of Organic Chemistry, both theoretical and applied The established utility of this structure theory, which is indeed a formulative hypothesis, is neither dependent upon the existence of atoms nor upon an intimate knowledge of the nature of valence or chemical affinity Similarly, the utility of this electronic conception of positive and negative valences, also a formulative hypothesis with the structure theory as its foundation, is not primarily dependent upon the existence or the possible isolation of electromers

The significance of this point of view may be more evident if some of the foregoing statements of Kekulé are paraphrased in modern terms In chemistry we have to decide whether the electronic conception of valence is an hypothesis adapted to the explanation of chemical and physico-chemical phenomena. More especially have we to determine whether or not the further development of electronic formulæ and the conceptions of electronic isomerism and tautomerism promise to advance our knowledge of the mechanism of chemical reactions. In view of the fact that electronic formulæ, in many instances, have proven to be more precise and more significant than the customary structural formulæ in the explanation of physical and chemical phenomena and the mechanism of reactions, it is quite conceivable that the electronic conception of valence may become a necessary adjunct to the structure theory This, of course, must depend upon the nature and extent of its applications and experimental verifications, and upon the part that should be played by just criticisms in bringing to light the relative merits and demerits of its applications The author hopes that these points of view will be constantly in the mind of the reader

CHAPTER II

THE ELECTRONIC CONCEPTION OF VALENCE

A. Fundamental Conceptions.

IN a lecture[1] on the Constitution of the Atom (Silliman Lectures, 1903), Sir J. J. Thomson formulated the electronic conception of positive and negative valences in the following words —

"On the view that the attraction between the atoms in a chemical compound is electrical in its origin, the ability of an element to enter into chemical combination depends upon its atom having the power of acquiring a charge of electricity. This, on the preceding view, implies either that the uncharged atom is unstable and has to lose one or more corpuscles before it can get into a steady state, or else that it is so stable that it can retain one or more additional corpuscles without any of the original corpuscles being driven out. If the range of stability is such that the atom, though stable when uncharged, becomes unstable when it receives an additional corpuscle, the atom will not be able to receive a charge either of positive or negative electricity, and will therefore not be able to enter into chemical combination. Such an atom would have the properties of the atoms of such elements as argon or helium.

"The view that the forces which bind together the atoms in the molecules of chemical compounds are electrical in their origin, was first proposed by Berzelius, it was also the view of Davy and of Faraday. Helmholtz, too, declared that the mightiest of chemical forces are electrical in their origin. Chemists in general seem, however, to have made little use of this idea, having apparently found the conception of 'bonds of affinity' more fruitful. This doctrine of bonds is, however, when regarded in one aspect almost identical with the electrical theory. The theory of bonds when represented graphically supposes that from each univalent atom a straight line (the symbol of a bond) proceeds, a bivalent atom is at the end of two such lines, a tervalent atom at the end of three, and so on , and that when the chemical compound is represented by a graphic formula in this way, each atom must be at the end of the proper number of the lines which represent the bonds Now, on the electrical view of chemical combination, a univalent atom has one unit charge, if we take as our unit of charge the charge on the corpuscle , the atom is therefore the beginning or end of one unit Faraday tube the beginning if the charge on the atom is positive, the end if the charge is negative A bivalent atom has two units of charge and therefore it is the origin or termination of two unit Faraday tubes Thus, if we interpret the 'bond' of the chemist as indicating a unit Faraday tube, connecting charged atoms in the molecule, the structural formulæ of the chemist can be at once translated into the electrical theory. There is, however, one point of difference which deserves a little consideration the symbol indicating a bond on the chemical theory is not regarded as having direction , no difference is made on this theory between one end of a bond and the other On the electrical theory, however, there is a difference between the ends, as one end corresponds to a positive, the other to a negative charge."

It is this earlier view of Sir J J Thomson that is most readily and significantly adaptable to chemical formulæ The conceptions presented in the foregoing quotation may be illustrated and amplified by applying them to the combination of two univalent atoms, X and Y, of such nature that X tends to lose a corpuscle, or electron, which Y tends to acquire Through the loss of one electron, i e , one unit negative charge (represented by the symbol $\ominus$), X functions *positively ,* thus, $X - \ominus \rightarrow \overset{+}{X}$ Through the acquisition of this electron, Y functions *negatively ,* thus, $Y + \ominus \rightarrow \overset{-}{Y}$

Accordingly, the electronic formula of the resultant compound, XY, from the union of $\overset{+}{X}$ and $\overset{-}{Y}$, is written $X\overset{+\;\;-}{\text{——}}Y$ which indicates the polarities of the bond of attraction or Faraday tube of force between X and Y

In this connection it is of interest to note that Baly and Desch[2] consider the labile hydrogen atom, in keto-enol tautomerism, to function as a potential ion "inasmuch as the bond of attraction or Faraday tube of force must be considered to be lengthened sufficiently to allow of the interchange of the atom from the one position to the other within the molecule." They also extend this view to salts in solution maintaining "that the bonds of attraction connecting the 'ions' together are lengthened by the solvent. When the length of the Faraday tubes is below a certain critical length, the salt is 'non-ionized.' When the average length of the tubes of force is equal to or a little less than the critical length, a few interchanges of ions between adjacent molecules takes place, and the salt is partially ionized. When the length of the Faraday tubes is greater than the critical value, then perfectly free interchange takes place between the ions of different molecules, and the salt is completely 'ionized.'"

From this point of view, the distinction between "electrolytes" and "non-electrolytes" is one of relation only; it depends upon the conditions which determine the critical lengths of the Faraday tubes between the constituent atoms of the substance.

Another phase of the electronic conception of valence has been presented by Sir William Ramsay[3] in his Presidential Address to the Chemical Society (1908). He advanced the hypothesis that electrons are atoms of the chemical element, electricity; they possess mass, form compounds with other elements, and serve as the bonds of union between atom and atom. He employed this idea of valence to explain the extrusion of ionizable groups in such compounds as the cobaltammine nitrites by further addition of ammonia. Such significant applications portend further development in the explanation of the mechanism of chemical changes.

A survey of these hypotheses leads to the conclusion, which is becoming more general, that, if the forces which hold the atoms together in electrolytes are electrical, then the same forces must also be assumed to hold in combination the atoms constituting the molecules of non-electrolytes. Hence, it may be maintained that chemical reactions which involve the dissociation of molecules, either of electrolytes or of non-electrolytes, are, let us say, *electronic*.

B. Electronic Formulæ of Diatomic Molecules

Passing from this general conclusion, consider briefly some of the electrochemical conceptions and facts that are related directly to the determination of the electronic formulæ of the diatomic molecules of certain elements.

In the first place, it is of historical interest to note that one of the chief causes contributing to the overthrow of the Dualistic System of Berzelius[4] was his failure to apply the conception of electro-dualism to the constitution of elementary molecules. This, however, was not the case with Helmholtz,[5] who, in his famous Faraday Lecture in 1881 applied an electrical conception of valence to the constitution not only of compound but also of elementary molecules These are his words "If we conclude from the facts that every unit of affinity is charged with one equivalent either of positive or of negative electricity, they can form compounds, being electrically neutral only if every unit charged positively unites under the influence of a mighty electric attraction with another unit charged negatively. . . The fact that even *elementary substances*, with few exceptions, have molecules composed of two atoms, make it probable that even in these cases electric neutralization is produced by the combination of two atoms, each charged with its full electric equivalent, not by neutralization of every single unit of affinity "

This conception of Helmholtz is stated conversely, in the modern phraseology of ionic dissociation, by W A. Noyes,[6] as follows "If we suppose what seems not to be improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of the molecules, it would follow that elementary molecules as well may ionize into positive and negative parts" Again, in this connection, Walden's researches[7] on conductivities of substances other than acids, bases and salts in different ionizing media, prove that the halogens, bromine and iodine, furnish not only anions, but cations as well $\overset{+}{\text{Br}}$ and $\overset{+++}{\text{Br}}$, $\overset{+}{\text{I}}$ and $\overset{+++}{\text{I}}$

Sir J J Thomson[8] states that this view "is also supported by the fact that when the molecules of an elementary gas are dissociated by heat, as in the case of iodine vapour, the electric conductivity of the dissociated gas is very high, showing that there are large quantities of both positive and negative ions present in the dissociated gas" Furthermore, "the numerous experiments which have been made on the dispersion of gases do not afford any evidence of the existence of any wide divergence between the dispersion of compound and elementary gases, hence we may conclude that if the atoms in the molecules of the compound gas are charged with electricity, the atoms in the molecules of elementary gases are also charged" Concurrently, the preceding facts indicate that the electronic formula and the electrolytic or electronic dissociation of a diatomic molecule (X_2) composed of univalent atoms may be represented by the following scheme:—

$$X_2 = \overset{+}{X}\text{——}\overset{-}{X} \rightleftharpoons \overset{+}{X} + \overset{-}{X}$$

C. Electronic Isomers or Electromers.

An extension of these ideas to the chemical union of two elementary gases, X_2 and Y_2, develops some new and fundamental conceptions Ordinarily, such a reaction is represented by the equation $X_2 + Y_2 \rightleftharpoons 2XY$, but in terms of electronic formulæ, combination, preceded by electronic dissociation, is represented by the following scheme —

$$\begin{array}{ccccccc}
X_2 & = & \overset{+}{X}\text{——}\overset{-}{X} & \rightleftharpoons & \overset{+}{X} & + & \overset{-}{X} \\
Y_2 & = & \overset{-}{Y}\text{——}\overset{+}{Y} & \rightleftharpoons & \overset{-}{Y} & + & \overset{+}{Y} \\
 & & & & \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright \\
 & & & & \overset{+}{X}\text{——}\overset{-}{Y} & & \overset{-}{X}\text{——}\overset{+}{Y}
\end{array}$$

Ordinarily only one structural formula is assigned to the compound XY, namely, X——Y, but, in the above scheme it is evident that XY may be represented by two different electronic formulæ, namely, $\overset{+}{X}\text{——}\overset{-}{Y}$ and $\overset{-}{X}\text{——}\overset{+}{Y}$ I have proposed the term *electronic isomer*, or more briefly, *electromer*[9] for this new type of isomer Several different electronic formulæ may be attributed to a given structural formula but this does not necessarily imply that the several electronic isomers or electromers are capable of independent existence Sir J J Thomson[10] foresaw the possibility of this new type of isomerism, and stated that even if such isomers were stable they would possess very different degrees of stability, and "it must be remembered that in considering the possibility of the existence of isomers from purely geometrical considerations, all questions as to stability are ignored, so that isomers which are indicated by geometry as possible may be dynamically unstable and thus incapable of preparation” Detailed evidence for the existence of electromers of the types $\overset{+}{X}\text{——}\overset{-}{Y}$ and $\overset{-}{X}\text{——}\overset{+}{Y}$ will be presented in subsequent chapters

D. Electronic Tautomerism.

The dynamic instability referred to above serves as the basis for another new conception, namely, that of *electronic tautomerism*[11] Tautomerism, in the usual sense, signifies an equilibrium mixture of ordinary structural isomers as, for instance, the well-known ketonic and enolic modifications Electronic tautomerism signifies an equilibrium mixture of two (or more) electromers in the sense that one electromer may be assumed to revert to another electromer through the transposition of valence electrons. This will effect a reversal of the polarity of certain atoms (or radicals) in the respective electromers as indicated in the following detailed scheme —

$$\overset{+}{X}\text{——}\overset{-}{Y} \rightleftharpoons \overset{+}{X} + \overset{-}{Y} \rightleftharpoons \overset{+}{X} + \ominus + Y \rightleftharpoons$$

$$X + Y \rightleftharpoons X + \ominus + \overset{+}{Y} \rightleftharpoons \overset{-}{X} + \overset{+}{Y} \rightleftharpoons \overset{-}{X}\text{——}\overset{+}{Y}$$

It should be noted that in the transition from electromer $\overset{+}{X}\,\overset{-}{Y}$ to $\overset{-}{X}\,\overset{+}{Y}$, or *vice versâ*, abbreviated thus

$$(\overset{+}{X}\text{——}\overset{-}{Y} \rightleftharpoons \overset{-}{X}\text{——}\overset{+}{Y}),$$

when $\overset{-}{Y}$ loses an electron, it becomes a neutral atom or radical, and $\overset{+}{X}$, acquiring this electron, or unit negative charge, also becomes a neutral atom or radical The intermediate existence of neutral atoms or radicals, X and Y, in the system of electronic tautomerism, furnishes a fundamental point of view for the interpretation of the existence and properties of “free radicals” (notably triphenyl-methyl and its derivatives) and the so-called “nascent state”. These features will be developed in subsequent chapters One of the purposes of this monograph is to show that many chemical reactions and their interpretation fully substantiate the principle of electronic tautomerism or the existence of electromers in dynamic equilibrium.

E. The Electronic Valence of an Atom.

It has been noted that a neutral atom (the valence in the neutral state is zero) may acquire one unit positive charge through the loss of one electron, or it may acquire one unit negative charge through the acquisition of one electron. Such a *univalent* atom may function, either as an independent ion or in chemical combination with another atom, in *two* distinct ways according as it is *positively* or *negatively univalent*. Thus, a *univalent* hydrogen atom may function as $\overset{+}{H}$ or as $\overset{-}{H}$, and the *univalent* chlorine atom as $\overset{+}{Cl}$ or as $\overset{-}{Cl}$.

Through (1) the gain or (2) the loss of two electrons, or (3) through the simultaneous loss of one electron and the gain of another electron, a *bivalent* atom may function in *three* distinct ways. Accordingly, its valences are respectively (1) both negative, or (2) both positive, or (3) one positive and one negative. Thus, a *bivalent* oxygen atom presents *three* types $\overset{--}{O}$, $\overset{++}{O}$, $\overset{+-}{O}$. Similarly, the *tervalent* nitrogen atom presents *four* types $\overset{+++}{N}$, $\overset{++-}{N}$, $\overset{+--}{N}$, and $\overset{---}{N}$. The *quadrivalent* carbon atom functions in *five* ways:—

$$\overset{++++}{C},\ \overset{+++-}{C},\ \overset{++--}{C},\ \overset{+---}{C},\ \text{and}\ \overset{----}{C}$$

It thus becomes evident that *an atom whose valence is (n) may function electronically in (n + 1) different ways.* This rule[12] is used in figuring the number of electronic formulæ which may be attributed to a given structural formula. Its application to the derivation of the electronic formula of benzene and other compounds is presented in detail later. In the meantime, it is expedient to illustrate this rule by a number of simple reactions and electronic formulæ, and, simultaneously, to consider the methods commonly employed in deriving the electronic formulæ of elements and compounds.

CHAPTER III

METHODS OF DEVELOPING ELECTRONIC FORMULÆ.

IT has been noted that electronic formulæ are virtually structural formulæ in which the bonds are qualified as having direction in the sense that one end of a bond corresponds to a positive, the other end to a negative charge The structural formula of a substance is derived through the consideration of three factors · (1) the number of atoms in the molecule, (2) the valence of each atom; and (3) the chemical and physical properties of the substance in question. As stated by Perkin and Kipping [13] "It is thus possible, with the help of valency considerations, to determine the state of combination of all the atoms of which the molecule is composed, and to express the results in a *structural formula;* this formula then not only shows the constitution or structure of the compound, but also summarizes in a concise and simple manner the more important chemical properties of the compound"

Now the conversion of a structural formula into an electronic formula by assigning positive and negative charges to the opposite ends of the bonds *is not an arbitrary procedure* it must be governed by a careful study of certain phenomena, notably (A) Ionization and Electrolysis, (B) Oxidation-reduction processes, and (C) Hydrolytic reactions *Each of these phenomena may be interpreted very aptly in terms of electric charges*, or, in other words, *in terms of positive and negative valences.* The correlation of these phenomena and principles makes the development of an electronic formula a consistent procedure. Simple illustrations of a general type may now be considered.

A. Ionization and Electrolysis.

In an aqueous solution, hydrogen chloride molecules by dissociation yield positive hydrogen and negative chlorine ions. The former migrate to the negative cathode while the latter move to the positive anode Hence the dissociating molecules of hydrogen chloride are qualified by the electronic formula $\overset{+}{\mathrm{H}}\text{——}\overset{-}{\mathrm{Cl}}$, and their electrolytic dissociation by the scheme $\overset{+}{\mathrm{H}}\text{——}\overset{-}{\mathrm{Cl}} \rightleftharpoons \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}}$.

This view does not preclude the possible existence, even in an aqueous solution, of negative hydrogen and positive chlorine ions The following illustration will show how, during electrolysis, negative hydrogen ions may be assumed to result by *cathodic reduction*, and positive chlorine ions arise by *anodic oxidation* a hydrogen atom carrying a unit positive charge may lose it on contact with the cathode, $\overset{+}{\mathrm{H}} + \ominus \rightarrow \mathrm{H}$ The resultant neutral atom immediately acquiring an electron from the cathode becomes a negative hydrogen ion, $\mathrm{H} + \ominus \rightarrow \overset{-}{\mathrm{H}}$, which is naturally repelled from the cathode and immediately combines with an approaching positive hydrogen ion to form a molecule of hydrogen, $\overset{-}{\mathrm{H}} + \overset{+}{\mathrm{H}} \rightarrow \overset{-}{\mathrm{H}}\text{——}\overset{+}{\mathrm{H}} = \mathrm{H}_2$

An analogous and simultaneous process may take place at the anode, in which case the negative chlorine ion gives up one electron to the anode thereby becoming a neutral atom, which through the loss of another electron becomes a positive chlorine atom The union of a positive and a negative chlorine ion yields the molecule $\overset{+}{\mathrm{Cl}}\text{——}\overset{-}{\mathrm{Cl}}$.

$$\overset{-}{\mathrm{Cl}} - \ominus \rightarrow \mathrm{Cl},\quad \mathrm{Cl} - \ominus \rightarrow \overset{+}{\mathrm{Cl}},$$
$$\overset{+}{\mathrm{Cl}} + \overset{-}{\mathrm{Cl}} \rightarrow \overset{+}{\mathrm{Cl}}\text{——}\overset{-}{\mathrm{Cl}} = \mathrm{Cl}_2.$$

This scheme leads to the definition of oxidation and reduction in terms of electrical charges or electrons

B. Oxidation and Reduction.

Anodic oxidation and cathodic reduction are effected by means of the electric current Electric currents may be produced by means of oxidation and reduction reactions Hence oxidation is generally considered to involve the acquisition of positive, or the loss of negative electrical charges, by atoms or ions, and, reduction involves the acquisition of negative, or the loss of positive charges Now since the electron is the unit negative charge of electricity, equivalent to the charge on a univalent ion, oxidation may be defined, in terms of the electronic conception, as the loss of electrons by atoms or ions, while reduction is the gain of electrons by atoms or ions.

The displacement of hydrogen from an acid by means of a metal is represented by an equation of the following type: M (a bivalent metal) + $2HX \rightarrow MX_2 + H_2$. The ionic equation for this reaction is $M + 2\overset{+}{H} \rightarrow \overset{++}{M} + H_2$. The metal, M, is oxidized to the bivalent ion, $\overset{++}{M}$, while the hydrogen ions, $2\overset{+}{H}$, are reduced to molecular hydrogen, H_2. A more detailed analysis of this change is presented in terms of the electronic conception according to the following scheme:—

$$M = \overset{+-}{M} \rightarrow \overset{++}{M} + 2\ominus,$$

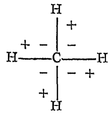
$$\overset{+}{H} + \ominus \rightarrow H,\quad H + \ominus \rightarrow \overset{-}{H},$$

$$\overset{+}{H} + \overset{-}{H} \rightarrow H\overset{+\quad -}{\text{———}}H = H_2$$

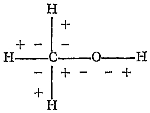
By way of explanation, an atom of the metal, M, is oxidized to the bivalent ion $\overset{++}{M}$ through the loss of two electrons, one of which reduces $\overset{+}{H}$, first, to neutral hydrogen, H. This neutral atom is then further reduced by the other electron to $\overset{-}{H}$. The union of $\overset{+}{H}$ and $\overset{-}{H}$ yields molecular hydrogen. This process closely resembles the *cathodic reduction* of positive hydrogen ions during the electrolysis of aqueous solutions of acids as previously noted.

These illustrations show that the number and the polarity of the charges of a given atom indicate its state of oxidation or reduction. Conversely, the state of oxidation of a given atom in a compound may be readily correlated with the electronic formula of the compound. The significance of this principle becomes more evident if attention is directed to the polarities of the valences of the carbon atom in five typical compounds, namely, (I) methane, (II) methyl alcohol, (III) formaldehyde, (IV) formic acid, (V.) carbonic acid and its anhydride, carbon dioxide.

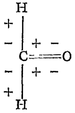
If, in these compounds, the hydrogen atoms function *positively* and the oxygen atoms are *negatively* bivalent, then the electronic formulæ of compounds I.-V. inclusive are written as follows —



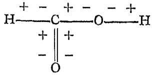
I



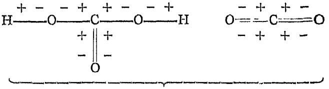
II



III



IV.



V

A rule has been stated, namely, that when the valence of an atom equals (n), that atom may function electronically, or in electronic formulæ, in ($n + 1$) different ways Since the carbon atom is *quadrivalent*, it functions in *five* different ways, thus—

$$\overset{-}{\underset{-}{-\,C\,-}} \qquad \overset{-}{\underset{-}{-\,C\,+}} \qquad \overset{-}{\underset{+}{-\,C\,+}} \qquad \overset{-}{\underset{+}{+\,C\,+}} \qquad \overset{+}{\underset{+}{+\,C\,+}}$$

$$\text{I} \qquad\quad \text{II} \qquad\quad \text{III} \qquad\quad \text{IV} \qquad\quad \text{V}$$

These types of carbon atoms (I -V) are embodied, respectively, in the preceding electronic formulæ of (I.) methane, (II) methyl alcohol, (III) formaldehyde, (IV) formic acid, and (V) carbonic acid Now since the acquirement of electrons or negative valences corresponds to reduction, and the loss of electrons, i e., the development of positive valences, corresponds to oxidation, it is at once evident that the above types and electronic formulæ (I -V inclusive) represent the successive stages of oxidation of the carbon atoms in the transitions from methane to carbon dioxide. In fact Bone has demonstrated that the slow combustion (i e , oxidation) of the hydrocarbon methane at temperatures below its ignition point, may be regarded as involving the successive formation of methyl alcohol, formaldehyde, formic acid, and finally, carbonic acid or carbon dioxide The electronic formulæ of these compounds afford an interpretation of these oxidations in terms of the positive and negative valences of the constituent atoms Such relationships as those noted in the preceding types (I -V) are made manifest, not by the ordinary structural formulæ, but only by the electronic formulæ of these five typical carbon compounds. In this way, the extensive field of oxidation-reduction reactions not only affords an experimental justification for the use of the electronic conception of positive and negative valences but also serves as one method of deriving electronic formulæ.

C. Hydrolytic Reactions

Another method of developing electronic formulæ and of correlating them with chemical properties is found in an electronic interpretation of hydrolytic reactions.

Granting that the hydrogen ion is positive and that the hydroxyl ion is negative under normal conditions, i.e., provided the hydrogen ion is not reduced and that the hydroxyl ion is not oxidized, and that, accordingly, the electronic formula of water is $H \overset{+\ \ -}{\text{——}} O \overset{-\ \ +}{\text{——}} H$, then it follows that *hydrolytic reactions afford an experimental method for ascertaining the polarity of the radicals of a compound under the particular conditions of the hydrolysis.*

The applicability of such a method both to electrolytes and to non-electrolytes is indicated by Abegg. "The observation that all reactions in which ions participate in measurable amounts—even the hydrolytic actions or the extremely weakly dissociated water—proceed to their equilibria with an immeasurably great velocity, has induced the assumption that indeed every capacity to react is to be attributed to the presence of ions. A basis for this assumption has been thought to exist in the fact that reactions between non-electrolytes usually proceed with extreme slowness corresponding to an immeasurably small, but not absolutely non-existent, dissociation." The method of applying hydrolytic reactions to the determination of the polarity of the radicals of either electrolytes or of non-electrolytes may be illustrated in general as follows.

If a compound, X.Y, on hydrolysis yields compounds of the types H.X and HO.Y, then X.Y is qualified by the electronic formula $X \overset{-\ \ +}{\text{——}} Y$. Its hydrolysis proceeds according to the scheme:—

$$X \overset{-\ \ +}{\text{——}} Y + H \overset{+\ \ -}{\text{——}} O \overset{-\ \ +}{\text{——}} H \rightarrow H \overset{+\ \ -}{\text{——}} X + H \overset{+\ \ -}{\text{——}} O \overset{-\ \ +}{\text{——}} Y,$$

or, more briefly

$$\overset{-}{X}\ \overset{+}{Y} + \overset{+}{H}\ \overset{-}{OH} \rightarrow \overset{+}{H}\ \overset{-}{X} + \overset{-}{HO}.\overset{+}{Y}$$

On the other hand, if the hydrolysis of X Y yields compounds H Y and HO X, then X Y is qualified by the electronic formula $\overset{+}{X}$——$\overset{-}{Y}$, the hydrolysis of which proceeds according to the abbreviated scheme :—

$$\overset{+}{X}\ \overset{-}{Y} + \overset{+}{H}\ \overset{-}{OH} \rightarrow \overset{+}{H}\ \overset{-}{Y} + \overset{-}{HO}\ \overset{+}{X}.$$

Thus, the products of hydrolysis of X Y indicate whether its electronic formula is $\overset{-}{X}\ \overset{+}{Y}$ or $\overset{+}{X}\ \overset{-}{Y}$.

In some instances, to be considered in detail later, a given compound, X Y, will yield four different products on hydrolysis, namely, H Y, HO X, H X, and HO Y In such instances, the conclusion is evident that the compound X Y must have functioned in two distinct ways, namely, as $\overset{+}{X}\ \overset{-}{Y}$ and $\overset{-}{X}\ \overset{+}{Y}$, or, in other words, X Y presents an example of electronic tautomerism ($\overset{+}{X}\ \overset{-}{Y} \rightleftharpoons \overset{-}{X}\ \overset{+}{Y}$) and interaction with water is virtually *two distinct hydrolytic reactions proceeding simultaneously* according to the general scheme —

$$(\overset{+}{X}\ \overset{-}{Y} \rightleftharpoons \overset{-}{X}\ \overset{+}{Y}) + \overset{+}{H}\ \overset{-}{OH} \begin{array}{l} \nearrow\ \overset{+}{H}\ \overset{-}{Y} + \overset{-}{HO}\ \overset{+}{X} \\ \searrow\ \overset{+}{H}\ \overset{-}{X} + \overset{-}{HO}\ \overset{+}{Y} \end{array}$$

This chapter has endeavoured to show that the development of an electronic formula, or the translation of a structural formula into an electronic formula, is made possible through the study and interpretation, in terms of positive and negative valences, of phenomena of ionization, oxidation-reduction processes and hydrolytic reactions The principles thus outlined will be illustrated fully in subsequent chapters with the purpose of making more apparent the enhanced significance of electronic formulæ.

CHAPTER IV

ELECTRONIC AMPHOTERISM

THE first rule relating to the positive and negative valencies of an element was proposed by Abegg and Bodlander[14] and subsequently by Abegg[15] These authors developed a theory of valency according to which any element manifests two kinds of valency—normal and contravalency—of opposite polarity. The former is the stronger and corresponds, as its name implies, to the accepted valencies of the element The normal valencies are usually positive in metals but negative in non-metals and the numerical value is equal to eight minus the number of contravalencies The Periodic Classification of the elements furnished the basis for the distribution of the normal and contravalencies

A few years later Friend[16] developed an electronic theory of positive and negative valence in which he distinguished between (1) free negative valency, (2) free positive valency, and (3) residual or latent valency

Friend defines the free negative valence of an element in terms of its capacity to combine with hydrogen "Since hydrogen is electro-positive and monovalent, only those elements which possess a negative valence can combine with it. As Ramsay has pointed out this is equivalent to saying that only those elements which are capable of receiving electrons can form hydrides". In addition to negative, some elements possess positive valency, that is to say, they are also able to part with electrons Such elements may be termed *amphoteric* Others apparently possess only positive or only negative valency.

Referring to free positive valency, Friend states that "the numerical value of the positive valency is not so easily determined as that of the negative, since we have no negative element corresponding with hydrogen, which combines with one atom of any other element in only one proportion". However, Friend suggests fluorine as the most suitable element for determining the maximum positive valency of the elements and maintains that "chlorine, fluorine, and oxygen are the only elements which possess free negative but no free positive valencies".

Finally, Friend's conception of residual or latent valency is quite similar to the "*neutral affinities*" of Spiegel and the *electrical double valencies* of Arrhenius, in that latent valencies can be called out in pairs of equal and opposite sign Thus, "In Ramsay's phraseology, this is equivalent to saying that when an element exerts its latent valency, it simultaneously parts with and receives, an electron. Consequently, the sum total of the electrons remains the same, and the electrochemical properties of the atom are unaltered"

I am constrained to maintain that the foregoing rules of positive and negative valencies as proposed by Abegg and Bodlander, and by Friend, may be replaced by a more general and more comprehensive rule, namely, that when the given valency of an element equals *n*, that element may function in $(n + 1)$ different ways This rule has been illustrated in the case of the quadrivalent carbon atom and its typical compounds In terms of this rule the univalent hydrogen atom may function in two ways, i e., either positively or negatively Accordingly, hydrogen in hydrogen chloride is positive and the electronic formula of the hydrogen chloride molecule is $\mathrm{H}\overset{+\quad -}{\text{——}}\mathrm{Cl}$; but, in sodium hydride, if sodium is positive, hydrogen must be negative, thus $\mathrm{Na}\overset{+\quad -}{\text{——}}\mathrm{H}$. This is in direct opposition to Friend's statement that "since hydrogen is electropositive and monovalent, only those elements which possess a negative valence can combine with it"

In like manner, univalent chlorine may function in two ways it is negative in hydrogen chloride but positive, as will be shown later, in hypochlorous acid, $\mathrm{H}\overset{+\quad -}{\text{——}}\mathrm{O}\overset{-\quad +}{\text{——}}\mathrm{Cl}$, and other compounds. This, too, is in opposition to Friend's statement[17] that "chlorine, fluorine, and oxygen are the only elements which possess free negative but no free positive valencies". Chlorine, at least, possesses positive valence as will be shown subsequently.

The capacity of a given element to lose and to acquire electrons and thereby function in various ways may be termed *electronic amphoterism.* It is now essential to subsequent developments to consider some instances in which the electronic amphoterism of hydrogen and chlorine is manifested. Since it is generally conceded that hydrogen normally functions positively while chlorine normally functions negatively, it will be of more particular interest to discuss the reactions and the electronic formulæ of a few simple compounds in which hydrogen is negative, and others in which chlorine is positive.

A. Negative Hydrogen

The conception of negative hydrogen is not new. Brodie,[18] in 1850, assumed the existence of a relation (polarity) between atoms entering into combination of such kind that one atom is distinguished as positive or negative as contrasted with the other. He represented the evolution of hydrogen which occurs when copper hydride is treated with hydrochloric acid, in terms of the old equivalents, thus—

$$\overset{+}{Cu_2}\overset{-}{H} + \overset{+}{H}\overset{-}{Cl} = \overset{+}{Cu_2}\overset{-}{Cl} + \overset{+}{H}\overset{-}{H}.$$

This is parallel to our present assumption that both copper hydride and molecular hydrogen may contain hydrogen atoms which function negatively.

It has been noted previously that negative hydrogen may result through cathodic reduction of positive hydrogen ions in the electrolysis of aqueous solutions of acids and precede the formation of molecular hydrogen. Likewise, it may be formed and precede the liberation of hydrogen when metals interact with acids or with water. Direct evidence of the existence of negative hydrogen is found in certain reactions of sodium hydride, and reference should be made to the interaction of sodium, on the one hand, and of sodium hydride on the other, with water according to equations (1) and (2), respectively:—

$$(1)\ 2Na + 2HOH \rightarrow 2NaOH + H_2$$
$$(2)\ NaH + HOH \rightarrow NaOH + H_2$$

From an ionic standpoint these reactions are represented thus:—

$$(1)\ 2Na + 2\overset{+}{H} \rightarrow 2\overset{+}{Na} + H_2,$$
$$(2)\ NaH + \overset{+}{H} \rightarrow \overset{+}{Na} + H_2$$

A further analysis of these reactions from an electronic point of view requires that a molecule of metallic sodium be regarded simply as a compound of a positive sodium ion with a negative electron, the interaction of which with water (i.e., with the positive hydrogen ions) corresponds to the following scheme:—

$$2\mathrm{Na} = 2\overset{+}{\mathrm{Na}}\ominus \rightleftharpoons 2\overset{+}{\mathrm{Na}} + 2\ominus$$

$$\overset{+}{\mathrm{H}} + \ominus \rightarrow \mathrm{H}, \quad \mathrm{H} + \ominus \rightarrow \overset{-}{\mathrm{H}};$$

$$\overset{+}{\mathrm{H}} + \overset{-}{\mathrm{H}} \rightarrow \overset{+}{\mathrm{H}}\!-\!\!-\!\overset{-}{\mathrm{H}} = \mathrm{H_2}$$

In other words, metallic sodium is oxidized to ionic sodium through the loss of electrons which reduce ionic hydrogen to the molecular state. Analogously, on the other hand, sodium hydride is a compound of positive sodium and negative hydrogen atoms, $\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{H}}$. Hence, the ionic equation (2) above is represented electronically as follows:—

$$\mathrm{Na\,H} = \overset{+}{\mathrm{Na}}\,\overset{-}{\mathrm{H}} \rightleftharpoons \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{H}}$$

$$\overset{+}{\mathrm{H}} + \overset{-}{\mathrm{H}} \rightarrow \overset{+}{\mathrm{H}}\,\overset{-}{\mathrm{H}} = \mathrm{H_2}$$

In other words, sodium hydride may be regarded as an ionogen which, on dissociation, yields positive sodium and negative hydrogen ions. The latter combine with positive hydrogen ions yielding molecular hydrogen.

Further evidence that the hydrogen of sodium hydride functions negatively is shown by the formation of sodium formate according to the equation—[19]

$$\mathrm{Na\,H} + \mathrm{CO_2} \rightarrow \mathrm{HCO_2Na}$$

An interpretation of this reaction from the electronic point of view shows it to be an oxidation-reduction process. It has been noted previously that each of the four valencies of the carbon atom in carbon dioxide is positive while in formic acid one of the carbon valences is negative and the other three are positive.* It follows, therefore, that when sodium hydride interacts with carbon dioxide, one of the four positive valences of the carbon atom is reduced to a negative valence through the reducing action of the negative hydrogen atom of sodium hydride. A detailed analysis of these changes may be indicated schematically as follows —

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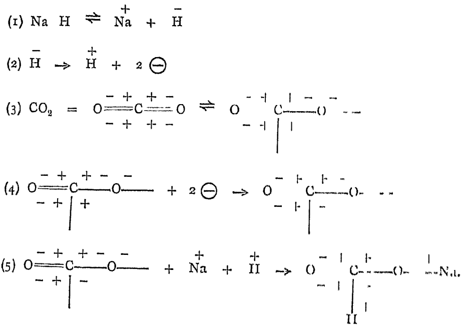
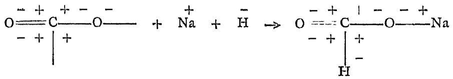
* See Electronic formulæ on p. 17.

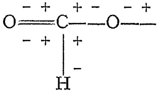
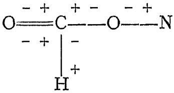


In (1), dissociation of NaH yields $\overset{+}{Na}$ and $\overset{-}{H}$. In (2), the unstable $\overset{-}{H}$ becomes $\overset{+}{H}$ through the loss of two electrons, 2⊖, and thereby acts as a reducing agent. Note that (3) illustrates the "opening up" of one of the double bonds of carbon dioxide presenting one free negative and one free positive valence, so to speak. In (4), the electrons, 2⊖, liberated in the transition of $\overset{-}{H}$ to $\overset{+}{H}$, effect the reduction of the free positive valence of carbon dioxide to a free negative valence. In (5), the union of $\overset{+}{Na}$ from (1), and of $\overset{+}{H}$ from (2), with the respective free negative valences of the oxygen and carbon atoms of carbon dioxide from (4), completes the electronic formula of sodium formate.

There is another scheme of interpreting the reaction in question. The dissociation of sodium hydride according to (1) into $\overset{+}{Na}$ and $\overset{-}{H}$, in conjunction with the opening up of the double bond in carbon dioxide, as noted in (3), makes possible the direct additions of $\overset{+}{Na}$ and $\overset{-}{H}$ to the free negative and the free positive valence, respectively, of carbon dioxide, thus :—



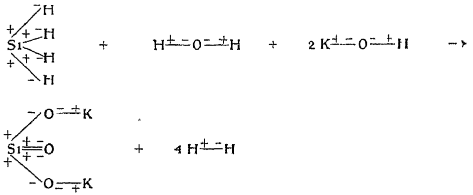
$$\mathrm{O}\underset{-\;+}{\overset{-\;+}{=\!=}}\mathrm{C}\underset{|\;+}{\overset{+\;-}{\text{——}}}\mathrm{O}\overset{-}{\text{——}} + \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{H}} \rightarrow \mathrm{O}\underset{-\;+}{\overset{-\;+}{=\!=}}\underset{\underset{\mathrm{H}}{|\,-}}{\mathrm{C}}\overset{+\;-}{\text{——}}\mathrm{O}\overset{-\;+}{\text{——}}\mathrm{Na}$$

The instability of $\overset{-}{H}$ and its tendency to revert to $\overset{+}{H}$ ($\overset{-}{H} \rightarrow \overset{+}{H} + 2\ominus$) with the loss of two electrons which reduce the positive carbon valence to a negative valence, is the occasion of the transition of the unstable electromer, containing negative hydrogen,  $\mathrm{O}\underset{-\;+}{\overset{-\;+}{=\!=}}\underset{\underset{\mathrm{H}}{|\,-}}{\mathrm{C}}\overset{+\;-}{\text{——}}\mathrm{O}\overset{-\;+}{\text{——}}\mathrm{Na}$, to the stable electromer,  $\mathrm{O}\underset{-\;+}{\overset{-\;+}{=\!=}}\underset{\underset{\mathrm{H}}{|\,+}}{\mathrm{C}}\overset{+\;-}{\text{——}}\mathrm{O}\overset{-\;+}{\text{——}}\mathrm{Na}$, sodium formate. It is at once evident that in the change from the unstable electromer ($\mathrm{NaO_2C}\overset{+\;\;-}{\text{——}}\mathrm{H}$) to the stable electromer ($\mathrm{NaO_2C}\overset{-\;\;+}{\text{——}}\mathrm{H}$), the $\overset{-}{H}$ of the former has been oxidized to $\overset{+}{H}$ in the latter, and, simultaneously, the positive carbon valence of the former electromer has been reduced to a negative valence in the latter. Hence this reversal of the polarity of the carbon-hydrogen valence affords an example of an *electronic intramolecular oxidation-reduction*. It should here be emphasized that any electronic intramolecular oxidation-reduction reaction virtually corresponds to the transition of one electromer to another ($X\overset{+\;\;-}{\text{——}}Y \rightleftharpoons X\overset{-\;\;+}{\text{——}}Y$) previously noted (p. 12) and defined as electronic tautomerism. Whether one electromer, or the other, or both, are the products of a given reaction will depend upon certain conditions which will be considered later.

Naturally it would be expected that the hydrides of strongly electropositive metals, such as sodium, contain negative hydrogen, as has been shown. It is interesting and significant to note that the hydride of the *non-metal silicon* also functions as a compound of negative hydrogen This is attested by the interaction (hydrolysis) of silicon hydride and aqueous potassium hydroxide One volume of the former yields in alkaline solution four volumes of hydrogen according to the equation—

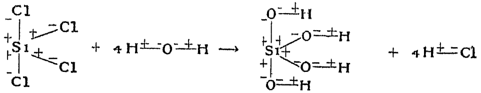
$$SiH_4 \ + \ HOH \ + \ 2KOH \ \rightarrow \ K_2SiO_3 \ + \ 4H_2$$

Now, potassium silicate is analogous in composition to potassium carbonate, a derivative of carbonic acid in which each of the valences of the carbon atom is positive Accordingly, each of the valences of the silicon atom in potassium silicate is assumed to be positive Furthermore, since neither water nor potassium hydroxide acts as a reducing agent in the above equation, it must also be concluded that each of the valences of the silicon atom in silicon hydride is positive Hence the hydrogen atoms of silicon hydride function negatively and the above reaction from the electronic standpoint is represented as follows —

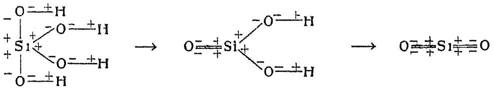


In this connection it is worthy of note that silicon and carbon, from the standpoint of the periodic classification, belong to the same natural family Since the non-metal silicon may be united to negative hydrogen as shown above, it is natural to conclude that *carbon atoms also may hold in combination negatively functioning hydrogen atoms* This condition will be met in the *electronic formula of benzene* That three of the hydrogen atoms of the benzene molecule, C_6H_6, function negatively while the other three function positively will be considered fully in subsequent chapters

In analogy with the hydrolysis of silicon hydride, silicon tetrachloride is also completely hydrolyzed in accordance with the scheme —



Since chlorine is negative in hydrogen chloride, it follows that the chlorine atoms in silicon tetrachloride are also negative Of course, the hypothetical ortho-silicic acid loses water yielding meta-silicic acid, which in turn gives the anhydride, silicon dioxide —



In silicon hydride and silicon tetrachloride, hydrogen and chlorine respectively function *negatively* Compounds and reactions will now be considered in which chlorine functions *positively*

B. Positive Chlorine.

It has been noted (p 15) that positive chlorine ions may arise during the electrolysis of hydrochloric acid through anodic oxidation of negative chlorine ions and precede the formation of molecular chlorine Apart from the phenomena of electrolysis, positive chlorine ions may exist and as such function in the production of hypochlorous acid through the interaction (reversible) of chlorine and water according to the equation,

$$\mathrm{Cl_2} + \mathrm{HOH} \rightleftharpoons \mathrm{HCl} + \mathrm{HOCl},$$

which is represented ionically and in terms of electronic formulæ as follows .—

$$\begin{array}{ccccccc}
\mathrm{Cl_2} & = & \mathrm{Cl}\overset{-\ \ +}{\text{———}}\mathrm{Cl} & \rightleftharpoons & \overset{-}{\mathrm{Cl}} & + & \overset{+}{\mathrm{Cl}} \\
\mathrm{HOH} & = & \mathrm{H}\overset{+\ \ -}{\text{——}}\mathrm{O}\overset{-\ \ +}{\text{——}}\mathrm{H} & \rightleftharpoons & \overset{+}{\mathrm{H}} & + & \mathrm{H}\overset{+\ \ -}{\text{——}}\mathrm{O}\overset{-}{\text{——}} \\
 & & & & \Updownarrow & & \Updownarrow \\
 & & & & \mathrm{H}\overset{+\ \ -}{\text{——}}\mathrm{Cl} & & \mathrm{H}\overset{+\ \ -}{\text{——}}\mathrm{O}\overset{-\ \ +}{\text{——}}\mathrm{Cl}
\end{array}$$

The chlorine atom in hypochlorous acid is *positive* and the *instability of hypochlorous acid and its oxidizing properties* may be attributed to *the tendency of positive chlorine to revert to the more stable negative chlorine* It has been shown that negative hydrogen acts as a reducing agent through the loss of electrons and thereby reverts to positive hydrogen $\overset{-}{H} - 2\ominus \rightarrow \overset{+}{H}$ On the other hand, positive chlorine acts as an oxidizing agent through the acquisition of electrons and thereby reverts to negative chlorine —

$$\overset{+}{Cl} + 2\ominus \rightarrow \overset{-}{Cl}$$

The decomposition (accelerated by the action of light) of dilute aqueous solutions of hypochlorous acid, yielding free oxygen and hydrochloric acid, according to the equation, $2HOCl \rightarrow 2HCl + O_2$, may be interpreted ionically and electronically as follows —

$$(1)\quad H\overset{+\;\;-}{\text{——}}O\overset{-\;\;+}{\text{——}}Cl \rightleftharpoons \overset{+}{H} + \overset{--}{O} + \overset{+}{Cl}.$$

$$(2)\quad \overset{--}{O} \rightarrow \overset{+-}{O} + 2\ominus$$

$$(3)\quad \overset{+}{Cl} + 2\ominus \rightarrow \overset{-}{Cl}$$

$$(4)\quad \overset{-}{Cl} + \overset{+}{H} \rightarrow H\overset{+\;\;-}{\text{——}}Cl$$

Equation (1) indicates complete ionic dissociation of hypochlorous acid. In (2) the oxygen ion through the loss of two electrons is oxidized to the atomic or electrically neutral state $\overset{+-}{O}$, or O This oxidation is effected by the positive chlorine ion, $\overset{+}{Cl}$, which through the acquisition of two electrons becomes a negative chlorine ion as noted in (3) In (4) the resultant negative chlorine ion unites with the positive hydrogen ion from (1), to give hydrogen chloride. This detailed interpretation may be abbreviated to conform to the scheme of an intramolecular oxidation-reduction reaction —

$$2H\overset{+\;\;-}{\text{——}}O\overset{-\;\;+}{\text{——}}Cl \rightarrow 2H\overset{+\;\;-}{\text{——}}O\overset{+\;\;-}{\text{——}}Cl \rightarrow$$

$$\left[2\overset{+}{H} + 2\overset{-}{Cl} + 2\overset{+-}{O}\right] \rightarrow 2H\overset{+\;\;-}{\text{——}}Cl + O\underset{-\;\;+}{\overset{+\;\;-}{=\!=}}O.$$

first electromer, $\text{H}\overset{+\quad -}{\text{———}}\text{O}\overset{-\quad +}{\text{———}}\text{Cl}$, is converted to the second romer $\text{H}\overset{+\quad -}{\text{———}}\text{O}\overset{+\quad -}{\text{———}}\text{Cl}$, through the reduction of $\overset{+}{\text{Cl}}$ to $\overset{-}{\text{Cl}}$ the concomitant oxidation of $\overset{-\,-}{\text{O}}$ to $\overset{-\,+}{\text{O}}$ The second elec- er, $\text{H}\overset{+\quad -}{\text{———}}\text{O}\overset{+\quad -}{\text{———}}\text{Cl}$, yields $\text{H}\overset{+\quad -}{\text{———}}\text{Cl}$ and molecular oxygen, $\underset{+}{\overset{-}{=}}\text{O}$ Another electronic formula for oxygen is possible, ely, $\text{O}\underset{+\quad -}{\overset{+\quad -}{=\!=\!=}}\text{O}$, but it is irrelevant to the explanation which ula is assigned to molecular oxygen.

n presenting these interpretations, it should be remembered it is no more possible to picture the absolute mechanism of emical change than it is to present a *final* explanation in ice. Each of the preceding interpretations of the decomposi- of hypochlorous acid involves one and the same fundamental ciple, namely, the transition of positive chlorine to negative rine through the loss of electrons. Furthermore, this transi- serves to explain the oxidizing action of hypochlorous acid some reactions (to be described later) hypochlorous acid ds, through dissociation, negative hydroxyl and positive ine ions —

$$\text{H}\overset{+\quad -}{\text{———}}\text{O}\overset{-\quad +}{\text{———}}\text{Cl} \rightleftharpoons \overset{-}{\text{HO}} + \overset{+}{\text{Cl}}$$

dation is effected through the reduction of $\overset{+}{\text{Cl}}$ to $\overset{-}{\text{Cl}}$ as noted ve In other reactions, hypochlorous acid undergoes intra- ecular oxidation-reduction and yields neutral or atomic (the alled "nascent") oxygen, $\overset{+\,-}{\text{O}}$, which in turn effects oxidation ough its reduction to $\overset{-\,-}{\text{O}}$ In other words, positive chlorine or tral oxygen atoms effect oxidation through transitions (1) (2) respectively :—

$$(1)\quad \overset{+}{\text{Cl}} + 2\ominus \rightarrow \overset{-}{\text{Cl}}$$

$$(2)\quad \overset{+\,-}{\text{O}} + 2\ominus \rightarrow \overset{-\,-}{\text{O}}.$$

terms of the electronic conception of positive and negative

2 3

valences, transition (1) is fundamental to the decomposition of hypochlorous acid and to its action as an oxidizing agent.

Since the acquisition of a given number of negative electrons is electrically equivalent to the loss of the same number of equivalent positive charges, transitions (1) and (2), respectively, may be indicated thus —

$$(1)\quad \overset{+}{\mathrm{Cl}} \rightarrow \overset{-}{\mathrm{Cl}} + 2\oplus$$

$$(2)\quad \overset{+-}{\mathrm{O}} \rightarrow \overset{--}{\mathrm{O}} + 2\oplus$$

Apropos of the electronic formula and properties of hypochlorous acid, the existence of positive chlorine ions is substantiated by the apparently anomalous fact that on electrolysis *concentrated solutions* of hydrochloric acid yield equal volumes of hydrogen and chlorine at cathode and anode respectively, but, on the other hand, *very dilute solutions* of the acid yield hydrogen at the cathode but no free chlorine at the anode Instead an equivalent amount of *oxygen* is evolved. Ostwald (10) states that "this is due to the fact that the water is decomposed by the chlorine with the formation of hydrogen chloride and oxygen according to the equation $2H_2O + 2Cl_2 = 4HCl + O_2$. This process, it is true, takes place with measurable velocity only in the light, we may, however, assume here, as in similar cases, that the process takes place without light, only very slowly." Ostwald's explanation should be modified and extended because he has not taken into account the fact that the liberation of oxygen from a solution of chlorine in water is due, most likely, to the intermediately formed hypochlorous acid according to the generally accepted equations —

$$2Cl_2 + 2HOH \rightleftharpoons 2HCl + 2HOCl,$$
$$2HOCl \rightarrow 2HCl + O_2.$$

In view of the electronic interpretation of the liberation of oxygen from hypochlorous acid, it follows that the evolution of oxygen at the anode during electrolysis of very dilute solutions of hydrochloric may be due to the following changes. Negative chlorine ions are oxidized at the anode to positive ions :—

$$\overset{-}{\mathrm{Cl}} \rightarrow \overset{+}{\mathrm{Cl}} + 2\ominus, \text{ or } \overset{-}{\mathrm{Cl}} + 2\oplus \rightarrow \overset{+}{\mathrm{Cl}}.$$

The dissociation of water, though extremely slight, yields hydrogen and hydroxyl ions which latter migrate to the anode and there encounter a much greater concentration of positive chlorine ions. The production of hypochlorous acid through the union of the negative hydroxyl and the positive chlorine ions, and its decomposition, as previously explained, fully accounts for the liberation of oxygen. Or, in equivalent terms, this change may readily take place through the oxidation of the hydroxyl ions by positive chlorine ions at the anode, thus —

$$\left.\begin{array}{l} 2\overset{-}{HO} \rightarrow 2\overset{+}{H} + 2\overset{--}{O} \\ 2\overset{+}{Cl} \rightarrow 2\overset{-}{Cl} + 4\oplus \end{array}\right\} \rightarrow 2\overset{+}{H}\text{——}\overset{-}{Cl} + O_2,$$

or summarized briefly,* $2\overset{-}{HO} + 2\overset{+}{Cl} \rightarrow 2\overset{+}{H} + 2\overset{-}{Cl} + O_2$

It is evident that this oxidation would proceed only in very dilute solutions of hydrochloric acid, i.e., in the presence of a very low concentration of hydrogen ions. Concentrated solutions of hydrochloric acid yield no oxygen on electrolysis because the high hydrogen ion concentration obliterates the hydroxyl ion concentration ($\overset{+}{H} + \overset{-}{OH} \rightarrow H_2O$). Hence in the absence of hydroxyl ions, the positive chlorine ions combine with the negative chlorine ions yielding molecular chlorine. In this way, the electronic conception of valence affords an interpretation of the apparently anomalous results obtained in the electrolysis of dilute and of concentrated solutions of hydrogen chloride.

C. Chloramines.

Not only hypochlorites but other compounds contain positive chlorine. Selivanow[22] noted the fact that the chloramines,

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* In simpler terms this change may be regarded, in a final analysis, as the action of positive chlorine ions upon negative oxygen ions —

$$2\overset{+}{Cl} + 2\overset{--}{O} \rightarrow 2\overset{-}{Cl} + O_2$$

In this connection it is noteworthy that Nernst[21] regards the action of chlorine upon oxygen ions, molecular oxygen being liberated, as analogous to the action of chlorine upon bromine ions, molecular bromine being liberated. In terms of electronic formulæ this latter change is reduced to the equation—

$$(Cl_2 = \overset{+}{Cl}\,.\,\overset{-}{Cl}) + 2\overset{-}{Br} \rightarrow (\overset{+}{Br}\,.\,\overset{-}{Br} = Br_2) + 2\overset{-}{Cl}.$$

RNHCl and R_2NCl, on hydrolysis and interaction with hydrogen iodide suffered replacement of their chlorine atoms, not by hydroxyl, but by hydrogen, and that two equivalents of iodine were liberated for each equivalent of replaced chlorine, thus

$$R_2NCl \;+\; 2HI \;\rightarrow\; R_2NH \;+\; HCl \;+\; I_2.$$

Selivanow attributed this remarkable reaction to the fact that the chlorine atom in chloramine existed as "hypochlorous chlorine" Accordingly, the above reaction is perfectly analogous to the action of hypochlorous acid upon hydrogen iodide —

$$HOCl \;+\; 2HI \;\rightarrow\; HOH \;+\; HCl \;+\; I_2.$$

In terms of electronic formulæ, *hypochlorous chlorine is positive chlorine,** and, therefore, the chloramine should yield positive chlorine on dissociation —

$$R_2NCl \;=\; R_2N\overset{-\;\;+}{\text{——}}Cl \;\rightleftharpoons\; R_2\overset{-}{N} \;+\; \overset{+}{Cl}.$$

Hence in the above reaction, $\overset{+}{Cl}$ oxidizes the negative iodine ion of the hydriodic acid to $\overset{+}{I}$ which in turn unites with $\overset{-}{I}$ to form molecular iodine An analysis and summary of these changes is given in the following scheme —

$$\overset{+}{Cl} \;+\; 2\ominus \;\rightarrow\; \overset{-}{Cl}$$
$$\overset{-}{I} \;-\; 2\ominus \;\rightarrow\; \overset{+}{I}$$
$$\overset{+}{I} \;+\; \overset{-}{I} \;\rightarrow\; (I\overset{+\;\;-}{\text{——}}I \;=\; I_2)$$
$$\overset{+}{Cl} \;+\; 2\overset{-}{I} \;\rightarrow\; \overset{-}{Cl} \;+\; I_2$$

Accordingly, the analogous reactions (1), and (2),

$$(1)\; R_2N\,.\,Cl \;+\; 2H\,.\,I \;\rightarrow\; R_2N\;H \;+\; H\;Cl \;+\; I_2,$$
$$(2)\; HO\;Cl \;+\; 2H\;I \;\rightarrow\; H\,.\,OH \;+\; H\;Cl \;+\; I_2,$$

are represented respectively in abbreviated electronic formulæ as follows —

$$(1)\; R_2\overset{-}{N}\,.\,\overset{+}{Cl} \;+\; 2\overset{+}{H}\,.\,\overset{-}{I} \;\rightarrow\; R_2\overset{-}{N}\,.\,\overset{+}{H} \;+\; \overset{+}{H}\,.\,\overset{-}{Cl} \;+\; \overset{+}{I}\,.\,\overset{-}{I}$$
$$(2)\; \overset{-}{HO}\;\overset{+}{Cl} \;+\; 2\overset{+}{H}\,.\,\overset{-}{I} \;\rightarrow\; \overset{-}{HO}\;\overset{+}{H} \;+\; \overset{+}{H}\;\overset{-}{Cl} \;+\; \overset{+}{I}\,.\,\overset{-}{I}.$$

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* The antiseptic action of Dakin's solution and his chloramines is undoubtedly due to positive chlorine.

Each of these reactions involves one and the same change, namely —

$$\overset{+}{Cl} + 2\overset{-}{I} \rightarrow \overset{-}{Cl} + I_2$$

The existence of positive chlorine in the chloramines is further attested by a reaction for their preparation, namely, the action of hypochlorous acid upon amines These reactions have been shown to be reversible —

$$R_2\overset{-}{N}.\overset{+}{H} + H\overset{-}{O}.\overset{+}{Cl} \rightleftharpoons R_2\overset{-}{N}\ \overset{+}{Cl} + \overset{+}{H}.\overset{-}{OH}.$$

Furthermore, molecular chlorine is liberated when the chloramines interact with hydrogen chloride :—

$$R_2\overset{-}{N}\ \overset{+}{Cl} + \overset{+}{H}\ \overset{-}{Cl} \rightleftharpoons R_2\overset{-}{N}.\overset{+}{H} + (\overset{+}{Cl}.\overset{-}{Cl} = Cl_2)$$

Other remarkable properties of the chloramines which have a direct bearing upon the constitution and electronic formula of benzene will be considered later

D. Positive Bromine, Iodine, and Cyanogen.

Halogens other than chlorine manifest the property of electronic amphoterism This is shown by a number of hydrolytic reactions Thus tetrabromomethane and tetraiodomethane yield bromoform and iodoform respectively :—

$$Br_3\overset{-}{C}.\overset{+}{Br} + \overset{+}{H}.\overset{-}{OH} \rightarrow Br_3\overset{-}{C}\ \overset{+}{H} + H\overset{-}{O}.\overset{+}{Br}$$

$$I_3\overset{-}{C}\ \overset{+}{I} + \overset{+}{H}\ \overset{-}{OH} \rightarrow I_3\overset{-}{C}.\overset{+}{H} + H\overset{-}{O}\ \overset{+}{I}.$$

Hypobromous and hypoiodous acids respectively embody positive bromine and positive iodine.

Iodine monochloride yields hydrogen chloride and hypoiodous acid in which chlorine and iodine are respectively negative and positive —

$$\overset{+}{I}.\overset{-}{Cl} + \overset{+}{H}\ \overset{-}{OH} \rightarrow \overset{+}{H}.\overset{-}{Cl} + H\overset{-}{O}.\overset{+}{I}$$

Nef's[23] observations that (1) chlorocyanogen yields hydrogen chloride and cyanic acid, while (2) iodocyanogen gives hypoiodous and prussic acid, show that the cyanogen radical, similarly to the halogen atoms, may function either positively or negatively :—

$$(1)\ \overset{-}{Cl}\ \overset{+}{CN} + \overset{+}{H}.\overset{-}{OH} \rightarrow \overset{+}{H}\ \overset{-}{Cl} + H\overset{-}{O}\ \overset{+}{CN}.$$

$$(2)\ \overset{+}{I}.\overset{-}{CN} + \overset{+}{H}.\overset{-}{OH} \rightarrow H\overset{-}{O}.\overset{+}{I} + \overset{+}{H}.\overset{-}{CN}.$$

Thus, there are numerous instances amongst compounds classed as non-electrolytes in which polarity of atoms and radicals is definitely manifested. These examples are readily interpreted and correlated in terms of the electronic conception of positive and negative valences The reactions just cited are but a few of the noteworthy examples of electronic amphoterism. Ordinary equations and customary formulæ do not reveal the significance of these relationships.

CHAPTER V

THE NASCENT STATE

THE so-called "nascent state" is intimately related to, and may be interpreted in terms of electronic amphoterism. Nascent action, according to common usage, is a term[24] for "all those phenomena in which a substance at the moment of its liberation from compounds performs reactions it is incapable of in its ordinary condition". Thus, to cite a simple and well-known case hydrogen has no action on silver chloride suspended in a liquid through which it is bubbled, hydrogen evolved within the liquid, *electrolytically* or *by action of metals*, produces metallic silver, hydrochloric acid being formed at the same time.

Concerning the various interpretations which have been proposed for such reactions, Alexander Smith[25] writes as follows "The term nascent hydrogen is used in different senses in a very confusing way. (1) It may mean nascent, literally, that is, newly born or liberated. (2) It is used also to mean different-from-ordinary, or, in fact, an allotropic form of hydrogen. (3) It is often limited to mean one particular allotrope, namely, atomic hydrogen. (4) It is used by Haber and others . to mean hydrogen activated by contact with a metal. (5) Finally, its activity is explained as being due to the larger amount of free energy contained in zinc plus acid plus reducing agent, as compared with the *free* hydrogen plus reducing agent. The last is identical with the explanation of the activity of oxidizing agents. The word nascent is, of course, a misnomer, excepting in connection with (1)."

A more comprehensive and conciliatory view of the nascent state and of nascent action may be developed in terms of the electronic conceptions of oxidation and reduction. Ordinarily, hydrogen functions positively while chlorine functions negatively, but in certain compounds, or under special conditions, previously described, hydrogen may function negatively and chlorine positively. Furthermore, negative hydrogen has been shown to act as a reducing agent since it naturally tends to revert to its more stable state, positive hydrogen, through the liberation of electrons (1) —

$$(1)\ \overset{-}{\mathrm{H}} \rightarrow \overset{+}{\mathrm{H}} + 2\ominus.$$

On the other hand, positive chlorine acts as an oxidizing agent, since it naturally tends to become negative by acquisition of electrons (2) —

$$(2)\ \overset{+}{\mathrm{Cl}} + 2\ominus \rightarrow \overset{-}{\mathrm{Cl}}$$

A closer analysis shows that *an electrically neutral state*, i.e., *the atomic state*, is a condition to be considered in the above transitions (1) and (2) This is shown in the following schemes (3) and (4) respectively —

$$(3)\ \overset{-}{\mathrm{H}} \rightarrow \mathrm{H} + \ominus,\ \mathrm{H} \rightarrow \overset{+}{\mathrm{H}} + \ominus$$

$$(4)\ \overset{+}{\mathrm{Cl}} + \ominus \rightarrow \mathrm{Cl},\ \mathrm{Cl} + \ominus \rightarrow \overset{-}{\mathrm{Cl}}$$

Now, if the atomic state and the nascent state are to be regarded as synonymous, then they may be defined, from the electronic standpoint, as an unstable condition which manifests not only an adaptability but also a tendency either to gain or to lose electrons and thereby attain a more stable condition. This tendency, however, *can not be limited to the atomic state of an element*, since not only atomic or neutral hydrogen, but also negative hydrogen tends to lose electrons. A survey of equations (1) and (3) indicates that a negative hydrogen atom may be more potent as a reducing factor than a neutral hydrogen atom since the former yields two electrons and the latter only one in the transition to the positive state. The activity of negative hydrogen as a reducing agent has been illustrated by the action of sodium hydride ($\overset{+}{\mathrm{Na}}\ \overset{-}{\mathrm{H}}$) upon carbon dioxide. The product of the reduction is sodium formate It may also be concluded that either negative or neutral hydrogen atoms produced at the cathode may function as the active reducing agent in the so-called electrolytic reductions

On the other hand, positive chlorine is a more potent oxidizing agent than is atomic or neutral chlorine since the former unit may combine with two electrons while the latter unites with only one in the transition to negative chlorine, as indicated in equations (2) and (4) above It has just been shown, in the preceding chapter, that the formation of positive chlorine ions at the anode would account for the liberation of oxygen during the electrolysis of very dilute solutions of hydrochloric acid (low hydrogen ion concentration) according to the abbreviated equation —

$$2\overset{+}{\mathrm{Cl}} + 2\overset{-}{\mathrm{OH}} \rightarrow 2\overset{+}{\mathrm{H}} + 2\overset{-}{\mathrm{Cl}} + \mathrm{O_2}$$

Therefore, from these briefly developed points of view, *the nascent state* may be defined more comprehensively as *an unstable condition of a substance which manifests both an adaptability and a tendency to lose electrons, or to gain electrons, and thereby revert to a more stable condition If the substance (ion, atom, or compound) loses electrons it acts as a reducing agent If it combines with electrons, it acts as an oxidizing agent* As a matter of fact, practically all actions classed as "nascent" are of an oxidation or a reduction type

This conception of the nascent state serves as the basis for an interpretation of the existence and the properties of "free radicals" to be fully considered in a later chapter It will be shown that *free radicals* may be defined as *electrically neutral atoms or molecules which are capable of developing either positive or negative valences* depending upon certain conditions which affect the loss or gain of electrons

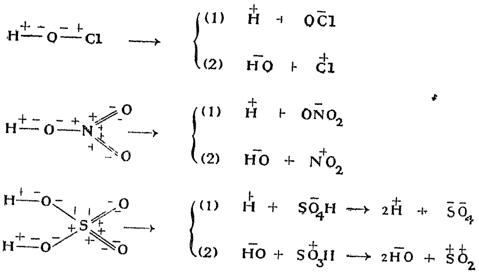
CHAPTER VI

IONIC AMPHOTERISM

ELEMENTS which gain or lose electrons and thereby function in different ways are termed amphoteric Compounds are designated as amphoteric when, through different modes of ionization, they function either as acids or as bases. Accordingly, *electronic amphoterism* relates to elements while *ionic amphoterism* relates to compounds It is essential to subsequent developments to consider briefly the phenomena of ionic amphoterism from the point of view of the electronic formulæ of amphoteric compounds

While hydrogen may function negatively and oxygen positively, it will be found that in the electronic formulæ of most compounds the hydrogen atoms manifest one positive valence while the oxygen atoms display two negative valences. The simplest illustration is that of water, $\text{H}\overset{+\ -}{\text{——}}\text{O}\overset{-\ +}{\text{——}}\text{H} \rightleftharpoons \overset{+}{\text{H}} + \overset{-}{\text{OH}}$ Though very slightly dissociated, water displays ionic amphoterism in yielding positive hydrogen ions, characteristic of all acids; and negative hydroxyl ions, typical of all bases. Thus, water has the unique distinction of functioning both as a very weak acid and a very weak base

Ionic amphoterism[26] is manifested by both acids and bases (metal hydroxides) Stieglitz[27] maintains that "pronounced amphoterism is shown by a large number of metal hydroxides; it is, perhaps the rule rather than the exception" It should be added that many acids also show pronounced ionic amphoterism as is evident from the distinctive types and products of interaction For example, hypochlorous, nitric, and sulphuric acids yield not only (1) positive hydrogen ions but also (2) negative hydroxyl ions. From this point of view, the electronic formulæ of these acids and their ionization, either (1) as an acid, or (2) as a base, respectively, are indicated in the following schemes.—



A general electronic formula may now be employed for each of these acids, namely, $\text{H}\overset{+\ -}{\text{——}}\text{O}\overset{-\ +}{\text{——}}\text{X}$, in which $\overset{+}{\text{X}} = \overset{+}{\text{Cl}}$, $\overset{+}{\text{NO}}_2$, or $\overset{+}{\text{SO}}_3\text{H}$

In neutralization reactions HOX, dissociating as an acid, interacts with bases, say NaOH, according to the ionic scheme for double decomposition reactions —

$$\begin{array}{ccccc}
\text{H}\overset{+\ -}{\text{——}}\text{O}\overset{-\ +}{\text{——}}\text{X} & \rightleftharpoons & \overset{+}{\text{H}} & + & \overset{-}{\text{OX}} \\
\text{Na}\overset{+\ -}{\text{——}}\text{O}\overset{-\ +}{\text{——}}\text{H} & \rightleftharpoons & \overset{-}{\text{HO}} & & \overset{+}{\text{Na}} \\
 & & \downarrow & & \downarrow \\
 & & \text{H}\overset{+\ -}{\text{——}}\text{O}\overset{-\ +}{\text{——}}\text{H} & & \text{Na}\overset{+\ -}{\text{——}}\text{O}\overset{-\ +}{\text{——}}\text{X}
\end{array}$$

On the other hand, when hypochlorous acid acts as a chlorinating agent, or when nitric acid acts as a nitrating agent, or when sulphuric acid functions as a sulphonating agent, the acids dissociate *as bases* The chlorination, nitration, or sulphonation of benzene likewise would conform to the ionic scheme for a double decomposition reaction ·—

$$\begin{array}{ccccc}
\text{H}\overset{+\ -}{\text{——}}\text{O}\overset{-\ +}{\text{——}}\text{X} & \rightleftharpoons & \overset{-}{\text{HO}}^{\bullet} & + & \overset{+}{\text{X}} \\
\overset{-}{\text{C}_6\text{H}_5}\,.\,\overset{+}{\text{H}} & \rightleftharpoons & \overset{+}{\text{H}} & + & \overset{-}{\text{C}_6\text{H}_5} \\
 & & \downarrow & & \downarrow \\
 & & \text{H}\overset{+\ -}{\text{——}}\text{O}\overset{-\ +}{\text{——}}\text{H} & & \text{C}_6\text{H}_5\overset{-\ +}{\text{——}}\text{X}
\end{array}$$

The preceding schemes illustrating (1) acid and (2) basic dissociation of HOX are summarized in the following reactions .—

$$(1)\ \overset{+}{H}\ \overset{-}{OX} + \overset{+}{Na}.\overset{-}{OH} \rightarrow \overset{+}{H}.\overset{-}{OH} + \overset{+}{Na}\ \overset{-}{OX}$$

$$(2)\ \overset{-}{HO}.\overset{+}{X} + \overset{-}{C_6H_5}.\overset{+}{H} \rightarrow \overset{+}{H}\ \overset{-}{OH} + \overset{-}{C_6H_5}\ \overset{+}{X}.$$

It should be noted that in direct substitution reactions, i.e., when X replaces H as in equation (2), $\overset{+}{X}$ usually replaces $\overset{+}{H}$. Such a change involves neither oxidation nor reduction. The substituent, however, may, subsequently, under certain conditions function negatively. In such instances (to be presented later) the compound C_6H_5 X manifests the phenomena of electronic tautomerism ($\overset{-}{C_6H_5}.\overset{+}{X} \rightleftharpoons \overset{+}{C_6H_5}\ \overset{-}{X}$)

The oxidizing action of certain oxygen acids is due undoubtedly to their capacity to ionize as bases.[25] The oxidizing action of hypochlorous acid has been explained in terms of its basic ionization, $HO.Cl \rightleftharpoons \overset{-}{HO} + \overset{+}{Cl}$, and the tendency of $\overset{+}{Cl}$ to revert to $\overset{-}{Cl}$, thus —

$$\overset{+}{Cl} + 2\ominus \rightarrow \overset{-}{Cl}.$$

The oxidizing action of nitric acid may be attributed to basic dissocation. For example, the oxidation of a ferrous salt is usually represented by the molecular equation —

$$2FeSO_4 + H_2SO_4 + 2HNO_3 \rightarrow Fe_2(SO_4)_3 + 2H_2O + 2NO_2.$$

If the nitric acid ionizes as a base, $\overset{-}{HO}\ \overset{+}{NO_2} \rightleftharpoons \overset{-}{HO} + \overset{+}{NO_2}$, then the above equation may be written ionically as follows:—

$$2\overset{++}{Fe} + 2\overset{--}{SO_4} + 2\overset{+}{H} + \overset{--}{SO_4} + 2\overset{-}{HO} + 2\overset{+}{NO_2} \rightarrow 2\overset{+++}{Fe} + 3\overset{--}{SO_4} + 2H_2O + 2NO_2$$

Eliminating the ions common to each side of the above reaction as well as the $\overset{+}{H}$ and $\overset{-}{OH}$ ions which form water, the following simple equation remains —

$$\overset{++}{Fe} + \overset{+}{NO_2} \rightarrow \overset{+++}{Fe} + NO_2.$$

The positive ion, $\overset{+}{NO_2}$ (resulting from the basic dissociation of nitric acid) is discharged by an electron from the ferrous ion, $\overset{++}{Fe}$. Accordingly, $\overset{+}{NO_2}$ is reduced to neutral or molecular

NO_2 which passes off as a brown gas. Concomitantly, $\overset{++}{Fe}$ is oxidized to $\overset{+++}{Fe}$ If sulphuric acid were not used in the above reactions, its part in supplying positive hydrogen ions would be played by the acidic ionization of the nitric acid.

As to sulphuric acid, when copper interacts with hot concentrated sulphuric acid according to the equation $Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$, one molecule of the sulphuric acid undergoes (1) acidic ionization, the other undergoes (2) basic ionization and (3) the metal copper becomes ionic through the loss of two electrons —

$$\begin{array}{llcccccc}
(1)\ H_2SO_4 & \rightarrow & 2\overset{+}{H} & + & \overset{--}{SO_4} & & \\
(2)\ (HO)_2SO_2 & \rightarrow & 2\overset{-}{HO} & & & + & \overset{++}{SO_2} \\
(3)\ Cu & \rightarrow & & & \overset{++}{Cu} & + & 2\ominus \\
\hline
\multicolumn{7}{c}{Cu + 2H_2SO_4 \rightarrow 2\overset{+}{H}\ \overset{-}{OH} + \overset{++}{Cu}.\overset{--}{SO_4} + SO_2.}
\end{array}$$

The positive ion, $\overset{++}{SO_2}$, is reduced to the neutral state and liberated as sulphur dioxide gas. Concomitantly, metallic copper is oxidized to the ionic state, $\overset{++}{Cu}$ The summation of (1), (2), and (3) gives the complete equation for the reaction.

Many other reactions are readily interpreted in terms of the ionic amphoterism of acids Subsequent applications of the conception of positive and negative valences will involve the principles of electronic and ionic amphoterism, and the nascent state as outlined in this and the preceding chapter

PART II.

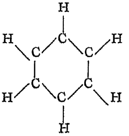
THE ELECTRONIC FORMULA OF BENZENE SUBSTITUTION IN THE BENZENE NUCLEUS

CHAPTER VII

THE CONSTITUTION OF BENZENE.

A. The Benzene Theory.

IN 1865 Kekulé[29] proposed his well-known formula for benzene, involving the assumptions that the six carbon atoms in benzene form a closed chain or *nucleus*, that the molecule is *symmetrical*, and that each carbon atom is directly united to one and only one atom of hydrogen These assumptions are embodied in the partial structural formula:—



which, however, does not take account of the fourth unit of valency of the carbon atoms in the nucleus. The disposition of the fourth valence has been the occasion of extended discussion and speculation

Since 1865 a variety of benzene formulæ have been proposed, foremost of which are the following the unsymmetrical formula of Sir James Dewar (1865), the diagonal formula of A Claus[30] (1867), the prismatic formula of A Ladenburg[31] (1869), the "centric formulæ" of H E Armstrong[32] (1887), and Baeyer[33] (1888) In addition to the foregoing plane formulæ, a number of stereochemical configurations of the benzene complex are noteworthy the octahedral formula of Julius Thomsen[34] (1886), W Vaubel's[35] configuration (1894); the Sachse[36] model (1888), the dynamic formulæ of J. N. Collie[37] (1897); and the device of B. Konig[38] (1905)

It is not the purpose of this monograph to discuss the characteristic features of the foregoing benzene theories. Their respective merits or demerits can be determined by a careful study of the references cited, which will reveal the fact that none of the proposed formulæ is accepted as complete H. E. Armstrong[39] summarizes the situation as follows · "The determination of the 'structure' of this hydrocarbon [benzene] has given rise to a large amount of paper warfare Two tendencies may be said to have been brought out in the course of the discussion on the one hand, the desire to arrive at a determination of the actual structure, on the other, the desire to devise formulæ which shall be faithful to the functional behaviour and broadly indicative of the structural relationship of the constituent elements The latter is perhaps the tendency which is now in the ascendant we are beginning to realize particularly in the case of carbon compounds that formulæ are primarily expressive of behaviour—being based on the observation of behaviour"

Notwithstanding these developments, we are still confronted with the fact that none of the proposed formulæ for benzene has lent itself to a uniform systematic explanation of substitution in the benzene nucleus and the many anomalous reactions of benzene and its derivatives. The foremost authority on the problem of substitution in the benzene nucleus, A F Holleman,[40] has recently written as follows "Notwithstanding the fact that the problem of substitution in the benzene nucleus has been studied intensively enough of late, there still remains a fundamental question which has not yet been solved, it is the question of knowing the reason why such or such group directs a new substituent chiefly to the para-ortho positions or chiefly to the meta position".

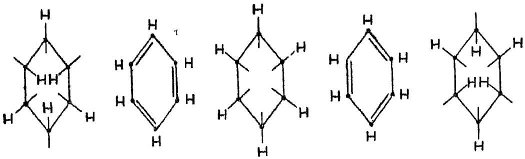
The great variety of benzene formulæ and their marked deficiencies in interpreting and correlating the behaviour of benzene and its derivatives, especially the substitution reactions, has led to the generally accepted conclusion that *the constitution of the benzene nucleus presents a remarkable case which must be dealt with in the formulation of any complete theory of valence.* Hence, a critical test of the utility of the electronic conception of positive and negative valences may be made by applying the principles developed in the preceding chapters to the constitution of the benzene nucleus. An electronic formula for benzene is thereby derived. No claim whatever is made that this electronic formula is the final solution to the manifold problem of the constitution of benzene, but it will be shown that the electronic formula of benzene and the underlying principles of the electronic conception of valence afford a means of interpreting and correlating many hitherto unexplained chemical, physico-chemical, and stereochemical problems presented by benzene and its derivatives.

B. The Electronic Formula of Benzene.

In the benzene formulæ proposed by Kekulé, Claus, Armstrong, and Baeyer, respectively, two of the units of valency of each of the six carbon atoms function in the formation of a closed homocyclic ring or "benzene nucleus". The third unit of valency engages a hydrogen atom The disposition of the fourth unit of valency led Kekulé to propose the existence of three "olefin" or double bonds in the ring. It is conceded that these are not of the same nature as the double bonds in the hydrocarbons of the olefin series In the Claus and Ladenburg formulæ, the fourth unit of valency, or bond, is represented as *directly* united to three other carbon atoms In the Armstrong and Baeyer "centric" formulæ the fourth unit of valency is directed towards a centre This signifies that the six carbon atoms of the ring have a general attraction for one another but they are not directly united in the usual way by the fourth unit of valency To what configuration, then, is the electronic conception of valence to be applied in order to derive an electronic formula for benzene? The configurations just noted are plane and static a comprehensive benzene configuration must be stereochemical and dynamic

In a discussion of the merits of the various space formulæ of benzene, Stewart[41] states that "the objections brought against the older types of space formulæ show that any advance in this branch of the subject must follow the lead given by Kekulé when he adopted the idea of a system in vibration as the best representation of the benzene molecule At the present day, the idea that benzene is one particular substance which can be represented at all times and under all conditions by the same rigid formula finds very few supporters among those who have studied the question thoroughly It is becoming generally recognized that the benzene molecule is in a state of continual vibration, and that the only satisfactory space formula will be one which represents all the other formulæ as phases of its own motions, and which may even suggest the possibility of new phases as yet unrecognized The main outlines of such a formula have been indicated by Collie,[42] and it seems probable that any space formulæ of benzene which may be proposed in the future will agree with his in essentials"

Collie's well-known space formula of benzene comprises a system of six carbon atoms (tetrahedra) each united to a hydrogen atom Movement in this system can take place in two ways (1) Movement of each tetrahedron about its centre, (2) movement of each tetrahedron about the centre of gravity of the whole system The plane projections of the symmetrical configurations rendered possible are represented by Collie as follows —



First phase Kekule's formula Centric formula Kekule's formula Last phase

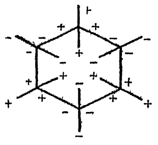
As stated by Stewart,[43] "this space formula for benzene, therefore, is in complete accord both with the Kekulé and the centric formula, showing that they are mutually convertible into one another It also shows how the supposed double linkages of the Kekulé formula shift between the carbon atoms, rendering the existence of two *o*-toluidines impossible But it differs from both in that in two out of five configurations there are two distinct sets of hydrogen atoms" The Collie formulæ are "in perfect accord with the formulæ of Ladenburg, Claus, or Dewar, or that of Baly, Edwards, and Stewart. This adaptability is not possessed in any degree by previous space formulæ, and it is this which makes the Collie formula superior to the others."

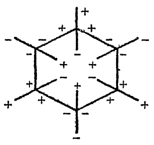
If this pre-eminence be granted to the Collie space formula, then it is the formula to which the electronic conception of valence should be applied in order to derive the most comprehensive electronic formula for benzene. In making this application it will be sufficient, for the present, to consider in detail the constituent atoms of only one of the five interconvertible phases of the plane projections of Collie's space formulæ, namely, the centric formula The derivation of an electronic formula from the centric formula will now be considered.

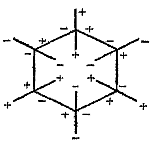
The quadrivalent carbon atom may function electronically in five different ways —

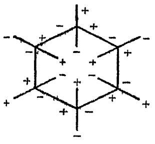
$$\begin{array}{ccccc} + & + & + & + & - \\ +\mathrm{C}+ & -\mathrm{C}+ & -\mathrm{C}+ & -\mathrm{C}- & -\mathrm{C}- \\ + & + & - & - & - \\ \text{I} & \text{II} & \text{III} & \text{IV} & \text{V.} \end{array}$$

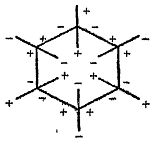
If benzene nuclei (centric formulæ) are composed of these several types of carbon atoms, each nucleus consisting of three pairs of the combined types I and V , II and IV., and III and III , symmetrically co-ordinated, then six and only six centric electronic formulæ, or electromers, are possible. They are as follows (A—F) —

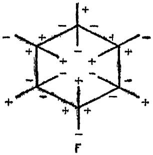

A


B

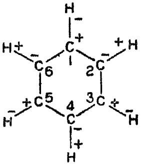

C


D


E


F

It has been noted that there are five plane projection formulæ of the Collie space formulæ for benzene of which the centric formula is one. Now since there are six centric electronic formulæ for benzene, (A—F), it follows that there are six times as many electronic formulæ for benzene as there are plane formulæ in the Collie system. If we disregard the double bonds of the Kekulé formulæ and the centric bonds of the centric formulæ, an abbreviated electronic formula for benzene is represented thus —



This formula is typical of each of the possible electronic formulæ or electromers of benzene While it has been derived in an *a priori* manner, so to speak, there are, nevertheless, pronounced reasons for its proposal. These reasons are embodied in the following distinctive characteristics.

(1) If the hydrogen atoms in positions 1, 3, and 5 are negative, those in positions 2, 4, and 6 are positive Or, since the electronic formula is perfectly symmetrical, if the hydrogen atoms in positions 1, 3, and 5 function positively, then those in positions 2, 4, and 6 function negatively

(2) The Kekulé and Centric formulæ of benzene fail to show any structural basis for the relationships existing between ortho- and para-positions in contradistinction to the meta-positions. The electronic formula shows at once that if a given hydrogen atom or substituent is negative, then those hydrogen atoms or substituents ortho and para to it are each positive, while those meta to it are each negative Or, if a given hydrogen atom or substituent is positive, then those atoms or substituents ortho and para to it are each negative, while those meta to it are each positive.

(3) From the foregoing, it is evident that the electronic formula for benzene presents, *per se*, the basis for a definite substitution rule, namely, *when substituents are of the same sign or polarity they will occupy positions which are meta to each other. if two substituents are of opposite sign or polarity they will occupy positions either ortho or para to each other*

(4) Collie's space formulæ for benzene, the plane projections of which have been noted, show, in two of the five phases, the existence of two sets of hydrogen atoms, namely, the 1, 3, 5- and the 2, 4, 6-set Concordantly, there exists in every electronic formula

for benzene a 1, 3, 5- and a 2, 4, 6-set of hydrogen atoms, the one set being of opposite sign or polarity to the other set The existence of two sets of hydrogen atoms enabled Collie to present a stereochemical explanation of the Crum Brown and Gibson Rule for the formation of di-substituted derivatives of benzene The electronic formula of benzene affords an entirely new interpretation of this rule and explains why certain mono-substituted derivatives of benzene yield chiefly ortho- and para-di-substituted compounds, while other mono-derivatives yield chiefly meta-di-substituted products Many other anomalous reactions of benzene and its derivatives find an interpretation in the electronic formula and the conception of positive and negative valence.

(5) The electronic formula of benzene in conjunction with the principle of electronic tautomerism affords an explanation of the *simultaneous* formation of ortho-, para-, and meta-substituted derivatives of benzene.

(6) The electronic formula of benzene permits the development of correlations with the additive and constitutive effects which are apparent in the molecular volumes of certain benzene derivatives

(7) Phenomena of light absorption and fluorescence are interpreted in terms of the existence of electromers in dynamic equilibrium

The electronic formulæ of benzene, naphthalene, anthracene, and phenanthrene, and the systems of dynamic equilibria of their various electromers will be presented in Part III, after the chemical properties of benzene and its derivatives have been fully considered

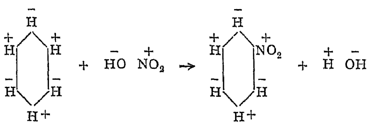
CHAPTER VIII

THE ANOMALOUS BEHAVIOUR OF SOME DERIVATIVES OF BENZENE.

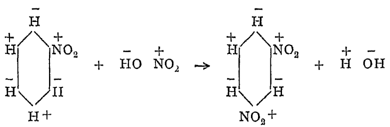
IT is the purpose of this chapter to show that many hitherto unexplained reactions of certain derivatives of benzene may be correlated with and interpreted in terms of the electronic formula of benzene and related conceptions of positive and negative valence

A. Ortho-, Para-, and Meta-Chloronitrobenzenes.

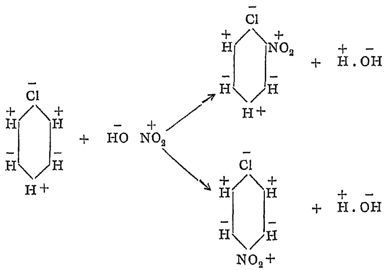
Why does (1) chlorobenzene, on nitration, yield only ortho- and para- chloronitrobenzenes while (2) nitrobenzene, on chlorination, yields only meta-chloronitrobenzene? Before an answer is proposed, it is expedient to consider the nitration of benzene. When benzene is directly nitrated, i e, interacts with $\overset{-}{\underline{HO}}\ \overset{+}{\underline{NO_2}}$, in which reaction nitric acid undergoes basic dissociation, mononitrobenzene is formed according to the electronic scheme —



The positive nitro radical of nitric acid replaces a positive hydrogen atom of the benzene nucleus. It is thus that *all direct substitution reactions effect the introduction of a positive substituent.* This positive substituent may, subsequently, function negatively according to the principle of electronic tautomerism, to be described fully in a later chapter. Now it is well known that mononitrobenzene on nitration yields *meta*-dinitrobenzene According to the electronic formula for mononitrobenzene the substitution of another positive nitro radical can take place in the *meta* position only since the positions meta to the nitro radical are occupied by positive hydrogen atoms. Hence the formation of meta-dinitrobenzene conforms to the electronic scheme:—

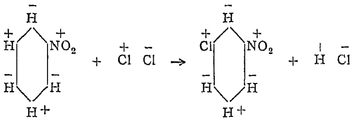


Having noted the electronic explanation of the nitration of benzene and of nitrobenzene, we can interpret (1) the nitration of chlorobenzene, and (2) the chlorination of nitrobenzene as follows. (1) Chlorobenzene, on nitration, yields ortho- and para-chloronitrobenzene. The electronic formula for benzene indicates that substituents occupying positions either ortho or para to each other are of opposite polarity. Nitration, as just noted, effects the substitution of a positive nitro radical. Therefore, the chlorine atom in chlorobenzene must be negative, otherwise ortho- and para-chloronitrobenzenes would not be formed. Thus, one concludes that the nitration of chlorobenzene conforms to the following electronic scheme in which the *positive* nitro radical assumes positions ortho and para to the *negative* chlorine atom:—



(2) On the other hand, nitrobenzene on chlorination yields only meta-chloronitrobenzene. The nitro radical in nitrobenzene is positive. The action of chlorine, $\overset{+}{\text{Cl}} . \overset{-}{\text{Cl}}$, upon nitrobenzene, a direct substitution, effects the introduction of a positive chlorine atom, the positive hydrogen atom thus replaced combines with

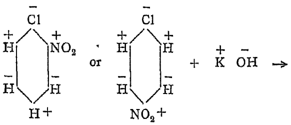
the negative chlorine atom yielding hydrogen chloride $\overset{+}{H}\ \overset{-}{Cl}$. According to the electronic formula of benzene the positive nitro radical and the positive chlorine atom, being of the same sign, must occupy positions meta to each other In fact, meta-chloronitrobenzene is the product of the chlorination reaction which conforms to the following electronic scheme —

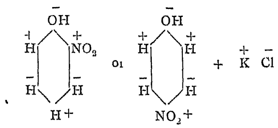


This reaction is perfectly similar to the nitration of nitrobenzene in each instance a meta-diderivative is formed

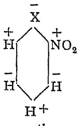
The interpretations of the preceding reactions (1) and (2), in terms of the electronic formula of benzene indicate that the chlorine atom is negative in ortho- and in para-chloronitrobenzene while in meta-chloronitrobenzene it is positive Is there any other experimental evidence to substantiate these electronic formulæ of ortho-, para-, and meta-chloronitrobenzenes?

The experimental verification is found in the apparently anomalous behaviour of ortho-, para-, and meta-chloronitrobenzenes when heated with alcoholic solutions of potassium hydroxide, $\overset{+}{K}\ \overset{-}{OH}$ The ortho and para compounds, *but not the meta*, are found to undergo complete hydrolysis, exchanging their chlorine atoms for the *negative* hydroxyl radical. Ortho- and para-nitrophenol and potassium chloride, $\overset{+}{K}\ \overset{-}{Cl}$, are the products of the reaction Therefore, the chlorine atoms in ortho- and para-chloronitrobenzenes are *negative* and their inter-reactions with potassium hydroxide takes place as follows —

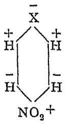




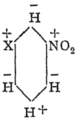
On the other hand, since meta-chloronitrobenzene does not exchange its chlorine atoms for *negative* hydroxyl, it follows that the chlorine atom in the meta compound is not negative Therefore, it is assumed to function positively (Further evidence that positive chlorine in the benzene nucleus resists removal in hydrolytic reactions is presented in Section C of this chapter) The bromonitrobenzenes are exactly similar in their behaviour to the chloronitrobenzenes Hence, the electronic formulæ for the chloro-, bromo-, and hydroxy-nitrobenzenes are summarized as follows (X = Cl, Br, or OH) —



ortho



para

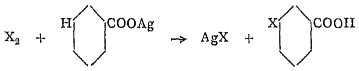


meta

The interpretations and correlations herewith presented in terms of electronic formulæ are not possible in terms of the ordinary structural formulæ commonly employed in the past

B. Action of Halogens upon Silver Benzoate.

Silver benzoate reacts readily with liquid bromine, and violently with iodine at a temperature of 150° The products are meta-bromo- and meta-iodobenzoic acids and silver bromide and iodide respectively (X = Br or I)



Why does the halogen atom which enters the ring assume a position meta to the carboxyl in preference to an ortho or para position? According to the electronic conception of positive and

THE
ELECTRONIC CONCEPT OF VALENCE AND THE CONSTITUTION OF BENZENE

BY

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WITH DIAGRAMS

LONGMANS, GREEN AND CO.
39 PATERNOSTER ROW, LONDON
FOURTH AVENUE & 30TH STREET, NEW YORK
BOMBAY, CALCUTTA, AND MADRAS
1921

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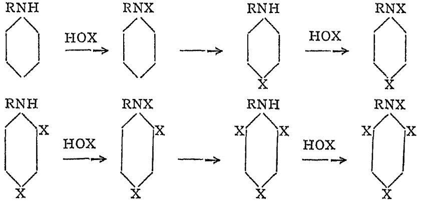
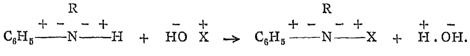
Therefore, the entering positive halogen atom, in substituting a positive hydrogen atom, must likewise occupy a position meta to the positive carboxyl radical This reaction and the electronic formula of benzene are thus correlated Furthermore, the dissociation of the halogen molecule into positive and negative parts, as indicated in the above equation, is a confirmation of the idea suggested at an earlier date by W A Noyes[41] that " if we suppose what seems not to be improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of the molecules, it would follow that elementary molecules as well may ionize into positive and negative parts"

C. Transference of Radicals from the Side-Chain to the Nucleus.

Various isomeric changes, stereochemical rearrangement reactions, may be explained in terms of the electronic conception of valence and the electronic formula of benzene The remarkable rearrangements characteristic of the substituted nitrogen halides investigated by Chattaway and Orton[45] are of particular interest. For example, acetanilide on treatment with hypochlorous acid yields phenylacetylnitrogenchloride which is readily transformed into *para*-chloroacetanilide This on treatment with hypochlorous acid gives para-chlorophenylacetylnitrogenchloride which is transformed into 2 4-dichloroacetanilide Proceeding thus, the final product is 2 · 4 6-trichloroacetanilide which will *not* undergo rearrangement These successive changes are summarized in the following scheme in which R = formyl, acetyl, or benzoyl, X = Cl or Br —

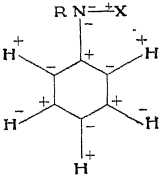


Why does the entering halogen atom invariably migrate to a position in the nucleus para or ortho to the amino group, provided these positions are unoccupied? Aniline as a derivative of ammonia, $\text{H}\overset{+\quad -}{\text{——}}\underset{\substack{|\,- \\ |\,+ \\ \text{H}}}{\text{N}}\overset{-\quad +}{\text{——}}\text{H}$, may be represented by the abbreviated electronic formula, $C_6H_5\overset{+\quad -}{\text{——}}NH_2$ The radical NH_2 is negative and accordingly must occupy the position of a negative hydrogen atom of the benzene nucleus The halogen atom in hypochlorous or hypobromous acid (X = Cl or Br), has been shown to function positively and its interaction with an anilide to conform to the reaction—



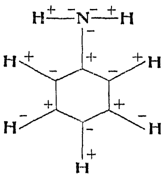
$$C_6H_5\overset{+\quad -}{\text{——}}\overset{R}{N}\overset{-\quad +}{\text{——}}H + \overset{-}{HO}\,\overset{+}{X} \rightarrow C_6H_5\overset{+\quad -}{\text{——}}\overset{R}{N}\overset{-\quad +}{\text{——}}X + \overset{+}{H}\,.\,\overset{-}{OH}.$$

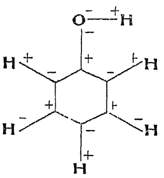
The following more comprehensive electronic formula for phenylacylnitrogenhalide follows —



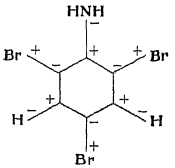
Therefore, in the process of transformation into a less labile isomeride, it is self evident that the *positive* halogen atom can exchange positions only with a positive hydrogen atom of the benzene nucleus, i e, in passing from the nitrogen atom to the nucleus it must assume either the para or ortho positions with respect to the attachment of the NH_2- or $RNH-$ radical which functions *negatively* When the para and both ortho positions are occupied, as in 2, 4, 6- tribromoacylnitrogenbromide, one finds that *rearrangement is theoretically impossible from the point of view of the electronic formula and it cannot be effected experimentally.* This two-fold conclusion constitutes a proof of the identity of polarity of the positions 2, 4, and 6, of the benzene nucleus, each of which is occupied by a positive chlorine atom in the trichloro- or tribromo-phenylacylnitrogenhalide Furthermore, the positive chlorine atoms of the nucleus resist hydrolysis and in this respect resemble the positive chlorine atom in metachloronitrobenzene which does not undergo hydrolysis On the other hand, recall that the chlorine atoms are negative in ortho and para chloronitrobenzenes which compounds are completely hydrolyzed yielding respectively ortho and para nitrophenols

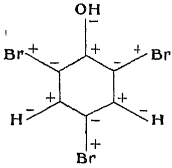
Aniline and phenol, on bromination, are quickly and quantitatively converted into 2, 4, 6- tribromoaniline and 2, 4, 6- tribromophenol, i e, the bromine atoms occupy positions in the nucleus ortho and para to the amino and hydroxyl radicals in the respective compounds These reactions are identical in their nature to the rearrangements which characterize the substituted nitrogen halides The explanation of these changes in terms of electronic formulæ are also identical in principle and method This follows from the exact similarity existing between the electronic formulæ of aniline and phenol —



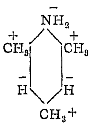


The negative amino radical of aniline and the negative hydroxyl radical of phenol each contains a positive hydrogen atom which is replaced by a positive bromine atom on interaction with free bromine or hypobromous acid On rearrangement, the positive bromine atom can assume only those positions in the nucleus which are occupied by positive hydrogen atoms *these are the positions ortho and para to the negative amino and the negative hydroxyl radicals.* Consequently, these substitutions and rearrangements, following in rapid succession, conform to the scheme indicated for the substituted nitrogen halides, the final products are 2, 4, 6- tribromoaniline and 2, 4, 6- tribromophenol —





Many other rearrangements involving transference of radicals from the side-chain to the nucleus, i e, from nitrogen to nuclear carbon, conform to the preceding interpretation. The following examples are noteworthy: Hofmann and Martins[46] found that the hydrochloride of aromatic methylamino compounds at 250°-350° suffered transference of the methyl group from the nitrogen to the ortho and para carbon atoms of the nucleus Thus, monomethylaniline yields ortho-toluidine and para-toluidine, and repetition of the process results finally in the formation of 2, 4, 6- cumidine —



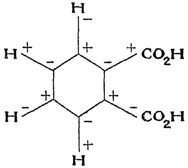
The nitrosamine of monomethylaniline, according to Fischer and Hepp[47] yields para-nitrosomethylaniline, and, in similar fashion, phenylnitramine, according to Bamberger,[48] changes to ortho- and para- nitraniline. The well-known benzidine and semidine conversions, and a variety of rearrangements to ortho and para positions encountered in the synthesis of many dye-stuffs conform to, and therefore, confirm the electronic formulæ of benzene and its substitution products It is electronic formulæ only which indicate the way in which these rearrangements take place ordinary structural formulæ do not lend themselves to an interpretation of these apparently anomalous reactions

D. Positive and Negative Carboxyl Radicals.

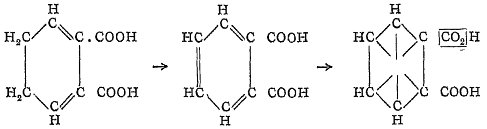
Some carboxyl radicals of certain derivatives of benzene readily suffer decomposition with the elimination of carbon dioxide —

$$R\,CO_2H \rightarrow R\,H + CO_2.$$

Other carboxyl radicals, under the same conditions, are quite stable May not this difference in stability be due to a difference in the polarity of the valence which binds the carboxyl radical to the benzene nucleus? Facts will now be considered which show that the polarity of the carboxyl radical has a definite influence upon the property of the compounds, or more particularly upon the stability of the carboxyl radical itself A compound containing two carboxyl radicals in positions ortho to each other is found in phthalic acid According to the electronic formula for benzene one of the carboxyl radicals of the acid should be positive while the other is negative as indicated in the formula —

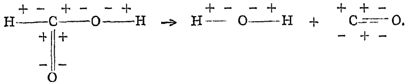


Is there any experimental evidence to justify this difference in the attachment of the carboxyl groups to the nucleus? Baeyer[49] has shown that the $\Delta^{3,5}$ $\Delta^{2,4}$, and $\Delta^{2,6}$ dihydrophthalic acids yield benzoic acid on oxidation. He attributes this to a shock (Erschutterung) to the a-carbon atom which causes it to lose carbon dioxide, this effect being associated with the change from ethylene to centric linkages, thus —



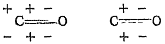
Bruhl,[50] in a critical examination of Baeyer's "Erschutterung Theory," asks why only one molecule instead of two molecules of carbon dioxide is removed from the acids in question, and has sought to explain the chemical behaviour of the dihydro acids on the simple basis of their difference of stability, which view has the advantage of being independent of any structural hypothesis But Bruhl, according to Cohen,[51] "fails to perceive that by avoiding any reference to structure as affecting stability, he is begging the question" It must then be concluded that up to the present time there is no satisfactory structural explanation as to why only one molecule of carbon dioxide instead of two is removed from the several dihydrophthalic acids investigated by Baeyer

The electronic formula of benzene requires that substituents occupying ortho positions to each other be of opposite polarity Consequently in the phthalic acids one carboxyl radical functions positively and the other negatively as previously indicated If reference be made to the electronic formulæ of formic and carbonic acids, it is evident that the carboxyl radical in formic acid is negative ($\mathrm{H}\overset{+\ -}{\text{——}}\mathrm{COOH}$) while in carbonic acid it is positive ($\mathrm{HO}\overset{-\ +}{\text{——}}\mathrm{COOH}$) Furthermore, in formic acid three of the valences of the carbon atom are positive and one is negative Accordingly, formic acid on decomposition ordinarily yields carbon monoxide and water —



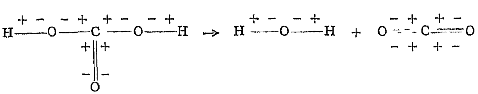
$$\mathrm{H}\overset{+\ -}{\text{——}}\underset{\substack{+\|+\\ -\|-\\ \mathrm{O}}}{\mathrm{C}}\overset{+\ -}{\text{——}}\mathrm{O}\overset{-\ +}{\text{——}}\mathrm{H} \rightarrow \mathrm{H}\overset{+\ -}{\text{——}}\mathrm{O}\overset{-\ +}{\text{——}}\mathrm{H} + \overset{+}{\underset{-}{\mathrm{C}}}\underset{+\ -}{\overset{+\ -}{\equiv}}\mathrm{O}.$$

The free positive and the free negative valence of the carbon atom in carbon monoxide become neutral In other words, carbon in carbon monoxide is bivalent —



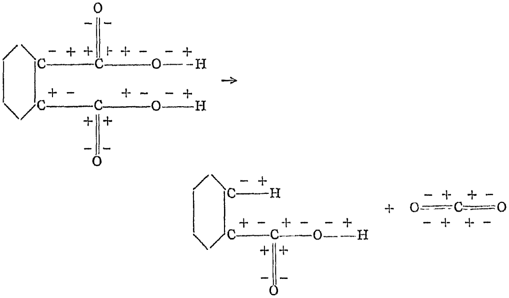
$$\overset{+}{\underset{-}{\mathrm{C}}}\underset{+\ -}{\overset{+\ -}{\equiv}}\mathrm{O} \qquad \mathrm{C}\underset{+\ -}{\overset{+\ -}{\equiv}}\mathrm{O}$$

On the other hand, in carbonic acid and its anhydride each of the four valences is positive Accordingly, carbonic acid on decomposition yields water and carbon dioxide —



$$\mathrm{H}\overset{+\ -}{\text{——}}\mathrm{O}\overset{-\ +}{\text{——}}\underset{\substack{+\|+\\ -\|-\\ \mathrm{O}}}{\mathrm{C}}\overset{+\ -}{\text{——}}\mathrm{O}\overset{-\ +}{\text{——}}\mathrm{H} \rightarrow \mathrm{H}\overset{+\ -}{\text{——}}\mathrm{O}\overset{-\ +}{\text{——}}\mathrm{H} + \mathrm{O}\underset{-\ +}{\overset{-\ +}{=}}\mathrm{C}\underset{+\ -}{\overset{+\ -}{=}}\mathrm{O}$$

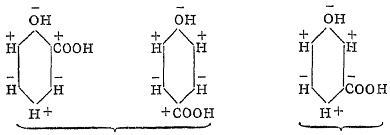
From the above it is evident that a carboxyl radical which is negative corresponds to the stage of oxidation represented by the carbon atom in formic acid, which does not lose carbon dioxide. On the other hand, a carboxyl radical which is positive corresponds to the stage of oxidation represented by the carbon atom in carbonic acid, which very readily loses carbon dioxide Therefore, the phthalic acids which embody a negative carboxyl radical and a positive carboxyl radical, lose only one molecule of carbon dioxide, a result of the decomposition of the positive carboxyl radical as indicated in the following scheme —



This explanation may now be extended to the interpretation of many other anomalous phenomena involving the liberation of carbon dioxide from various substituted benzoic acids

E. Elimination of Carbon Dioxide.

Cazeneuve[52] in a study of the decomposition of various hydroxybenzoic acids found that some of them readily lose carbon dioxide when heated with water or aniline, while others were quite stable. For instance, orthohydroxybenzoic acid (salicylic acid) when heated with aniline to 240° in a sealed tube gave phenol and carbon dioxide Parahydroxybenzoic acid likewise gave carbon dioxide but the meta acid suffered no change The instability of the ortho and the para acids and the stability of the meta acid may be interpreted in terms of the electronic formula of benzene and the polarity of the carboxyl radicals These radicals in ortho- and para-hydroxybenzoic acids must function positively, i e., they correspond to the state of oxidation represented by carbonic acid and therefore may yield carbon dioxide Furthermore, if the hydroxyl radical in the hydroxybenzoic acids is negative, then the electronic formulæ for the ortho- and para-hydroxybenzoic acids require that the carboxyl radicals be positive, while the carboxyl radical in the meta acid must be negative. The meta carboxyl radical being negative corresponds to the state of oxidation of formic acid and, therefore, does not lose carbon dioxide. The correlation of these phenomena with the conception of positive and negative valences is expressed in the following formulæ for ortho-, para-, and meta-hydroxybenzoic acids:—



(unstable lose carbon dioxide) (stable)

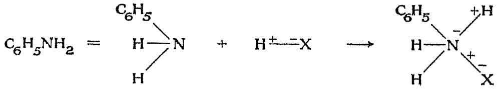
From the above, a general conclusion may be drawn, namely, that *a carboxyl radical either ortho or para to a negative radical is positive and, therefore, unstable, yielding carbon dioxide when heated with water or aniline.* On the other hand, *a carboxyl radical meta to a negative hydroxyl radical is also negative and, therefore, stable, not yielding carbon dioxide when heated with water or aniline.*

The above conclusion receives remarkable confirmation by the recent and numerous experiments of Hemmelmayr[53] in an extensive research "Concerning the influence of the nature and position of substituents upon the stability of the carboxyl radical in the substituted benzoic acids". Cazeneuve estimated the relative stability of the carboxyl radicals by comparing temperatures at which different compounds eliminated carbon dioxide. Hemmelmayr's method is more comprehensive, in that he heated weighed quantities of various acids with either 50 c.c. of water or 50 c.c. of aniline and estimated quantitatively the amounts of carbon dioxide liberated. In this manner he experimented with thirty-nine differently substituted hydroxybenzoic acids. Their behaviour in general conformed to the rule indicated above. In other words, an examination of the formula showed that every acid which contained a carboxyl radical either ortho or para to an hydroxyl radical yielded carbon dioxide. On the other hand, those acids in which the carboxyl group was neither ortho nor para, but only meta, to an hydroxyl radical did not yield carbon dioxide. Thirty-five of the thirty-nine variously substituted hydroxybenzoic acids conformed to this generalization. Among thirteen mono-, di-, and trihydroxybenzoic acids there was not one exception. Hence, it must be concluded that the electronic formula of benzene and the conception of positively and negatively functioning carboxyl radicals afford an interpretation of the anomalous behaviour of numerous and differently substituted hydroxybenzoic acids, some of which lose carbon dioxide while others do not.

While it is thus evident that positively functioning carboxyl radicals lose carbon dioxide when heated with water or aniline, nothing has been found in the literature which would indicate or explain the mechanism of these reactions.

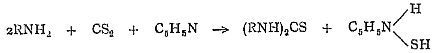
F. The Mechanism of the Elimination of Carbon Dioxide.

In attempting to explain the action of water or aniline it should be noted that each of these reagents which effect the elimination of carbon dioxide contains an unsaturated atom, i.e., oxygen may increase its valence from two to four while nitrogen, in aniline and other amines (or ammonia), may increase its valence from three to five. For instance, the combination of aniline with hydrogen halide may be represented as follows —

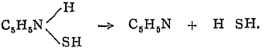


Since Hemmelmayr has found that amines other than aniline effect the elimination of carbon dioxide it is advisable now to limit this explanation to the unsaturated state of the nitrogen atom in amines.

In a recent paper [54] I have shown that the unsaturated nitrogen atom in the amine, pyridine, lends itself to the elimination of hydrogen sulphide in a new reaction for the preparation of thiocarbanilides, according to the equation—



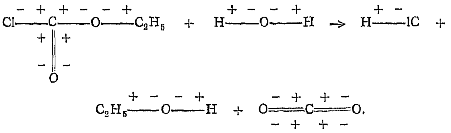
$$2RNH_2 + CS_2 + C_5H_5N \rightarrow (RNH)_2CS + C_5H_5N\begin{matrix}/H\\ \backslash SH\end{matrix}$$



$$C_5H_5N\begin{matrix}/H\\ \backslash SH\end{matrix} \rightarrow C_5H_5N + H\ SH.$$

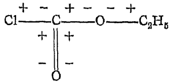
In other words pyridine combines with the elements of hydrogen sulphide forming the unstable pyridinium sulphide which, decomposing, regenerates the original pyridine and eliminates hydrogen sulphide Analogously, it may be assumed that *an unstable addition compound of an amine and the oxybenzoic acid is formed which, decomposing, regenerates the amine and liberates carbon dioxide*

The validity of this assumption was put to an experimental test by employing pyridine as the amine and chlorocarbonic ethylester as an analogue of an hydroxybenzoic acid. The possibility of the elimination of carbon dioxide from chlorocarbonic ethylester is warranted, since all of the valences of its carbon atom are positive and so correspond to the state of oxidation of the carbon atom in carbonic acid and carbon dioxide This follows from its interaction with water —



$$\overset{-}{Cl}—\underset{\substack{+\,\|\,+\\-\,\|\,-\\O}}{\overset{+\quad+}{C}}—\overset{-\;-}{O}—\overset{+}{C_2H_5} + \overset{+}{H}—\overset{-\;-}{O}—\overset{+}{H} \rightarrow \overset{+}{H}—\overset{-}{Cl} + \overset{+}{C_2H_5}—\overset{-\;-}{O}—\overset{+}{H} + \underset{-}{\overset{-}{O}}=\underset{+\;+}{\overset{+\;+}{C}}=\underset{-}{\overset{-}{O}}.$$

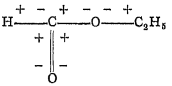
It should be noted, parenthetically, that chlorocarbonic ethylester is very frequently, but incorrectly, called "chloroformic ethylester" which implies that it is a derivative of formic acid If such were the case then its carbon atom must possess three positive valences and one negative valence in order that it correctly correspond to the state of oxidation of the carbon atom in formic acid Its electronic formula would then be as follows —



$$\overset{+}{Cl}—\underset{\substack{+\,\|\,+\\-\,\|\,-\\O}}{\overset{-\quad+}{C}}—\overset{-\;-}{O}—\overset{+}{C_2H_5}$$

This "electromer" if hydrolyzed could not yield carbon dioxide directly. The products would be hypochlorous acid,

$\overset{+}{\mathrm{H}}\text{——}\overset{-\ \ -}{\mathrm{O}}\text{——}\overset{+}{\mathrm{Cl}}$, and ethyl formate—



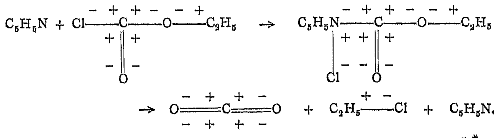
$$\overset{+}{\mathrm{H}}\text{——}\overset{-\ \ +}{\mathrm{C}}\text{——}\overset{-\ \ -}{\mathrm{O}}\text{——}\overset{+}{\mathrm{C_2H_5}}\quad (\mathrm{C}\overset{+\ +}{=}\overset{-\ -}{\mathrm{O}})$$

but, as just noted, this is not the case.

When chlorocarbonic ethylester is dissolved in an anhydrous solvent (carbon tetrachloride, benzene, or toluene) the addition of a like solution of pyridine yields at once an extremely unstable addition-compound (white solid, not yet isolated) which spontaneously decomposes, liberating carbon dioxide and ethyl chloride. Experiments were performed in order to determine quantitatively the extent of the decomposition of various amounts of chlorocarbonic ethylester by a fixed amount of pyridine. The results of these experiments are embodied in the following table, which presents the molecular ratios of the interacting substances, the quantities employed, the amount of carbon dioxide evolved and the corresponding percentages of the theoretical yields of carbon dioxide based upon the ratio CO_2 $ClCO_2C_2H_5$

Molecular Ratios	C_5H_5N (Grams)	$ClCO_2C_2H_5$ (Grams)	CO_2 (Grams)	Per Cent. of Theory
2 C_5H_5N 1 $ClCO_2C_2H_5$	3·95	2 71	0 9720	88 36
2 C_5H_5N 2 $ClCO_2C_2H_5$	3 95	5 42	1 8960	86 18
2 C_5H_5N 3 $ClCO_2C_2H_5$	3 95	8 13	2 7305	82 74

The reaction mixture in the flask still contained pyridine which effected the decomposition of additional quantities of chlorocarbonic ethylester. Hence it must be concluded that the pyridine acts as a catalytic agent in effecting the elimination of carbon dioxide from the ester through the intermediate formation of an unstable addition compound. The reactions involved may be represented by the following equations —

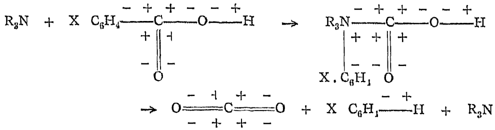


$$C_5H_5N + \overset{-}{\mathrm{Cl}}\text{——}\overset{+\ \ +}{\mathrm{C}}\text{——}\overset{-\ \ -}{\mathrm{O}}\text{——}\overset{+}{C_2H_5}\ (\mathrm{C}\overset{+\ +}{=}\overset{-\ -}{\mathrm{O}}) \rightarrow C_5H_5\overset{-}{\mathrm{N}}\text{——}\overset{+\ \ +}{\mathrm{C}}\text{——}\overset{-\ \ -}{\mathrm{O}}\text{——}\overset{+}{C_2H_5}\ (\mathrm{N}\overset{+\ -}{\text{—}}\mathrm{Cl},\ \mathrm{C}\overset{+\ -}{\text{—}}\mathrm{Cl},\ \mathrm{C}\overset{+\ +}{=}\overset{-\ -}{\mathrm{O}})$$

$$\rightarrow \overset{-}{\underset{-}{\mathrm{O}}}=\overset{+\ +}{\underset{+\ +}{\mathrm{C}}}=\overset{-}{\underset{-}{\mathrm{O}}} + \overset{+}{C_2H_5}\text{——}\overset{-}{\mathrm{Cl}} + C_5H_5N.$$

I have found that amines, other than pyridine, also effect the elimination of carbon dioxide from chlorocarbonic methyl-, ethyl-, and propyl- esters Hemmelmayr has found that amines other than aniline effect the elimination of carbon dioxide from various hydroxybenzoic acids in which the carboxyl radicals have been shown to function positively Therefore, equations perfectly analogous to those above may represent the action of an amine of the general formula R_3N upon an hydroxybenzoic acid (or any other substituted benzoic acid in which the carboxyl radical is positive) as follows (Equations showing the formation of the amine salts of the acids have been omitted as they are not essential to the principal changes involved)

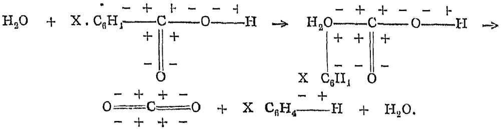
(R = Alkyl, aryl, or H, X = OH or other substituent)



$$R_3N + X\,C_6H_4\overset{-\ +}{\text{——}}\underset{\underset{O}{\overset{+\ +}{\underset{-\ -}{\|}}}}{C}\overset{+\ -}{\text{——}}O\overset{-\ +}{\text{——}}H \rightarrow R_3N\overset{-\ +}{\text{——}}\underset{\underset{\underset{O}{\overset{+\ +}{\underset{-\ -}{\|}}}}{}}{C}(\overset{+\ -}{|}X.C_6H_4)\overset{+\ -}{\text{——}}O\overset{-\ +}{\text{——}}H$$

$$\rightarrow \underset{-\ +}{\overset{-\ +}{O=\!=}}\underset{+\ -}{\overset{+\ -}{C=\!=}}O + X\,C_6H_4\overset{-\ +}{\text{——}}H + R_3N$$

The formation of an intermediate unstable compound of the amine and the acid depends upon an increase in the valence of the nitrogen from three to five Similarly, the action of water in effecting the elimination of carbon dioxide would depend upon the formation of an unstable oxonium compound through an increase in the valence of the oxygen atom from two to four as indicated in the following equations, which are perfectly analogous to those above —



$$H_2O + X.C_6H_4\overset{-\ +}{\text{——}}\underset{\underset{O}{\overset{+\ +}{\underset{-\ -}{\|}}}}{C}\overset{+\ -}{\text{——}}O\overset{-\ +}{\text{——}}H \rightarrow H_2O\overset{-\ +}{\text{——}}\underset{\underset{\underset{O}{\overset{+\ +}{\underset{-\ -}{\|}}}}{}}{C}(\overset{+\ -}{|}X\,C_6H_4)\overset{+\ -}{\text{——}}O\overset{-\ +}{\text{——}}H \rightarrow$$

$$\underset{-\ +}{\overset{-\ +}{O=\!=}}\underset{+\ -}{\overset{+\ -}{C=\!=}}O + X\,C_6H_4\overset{-\ +}{\text{——}}H + H_2O.$$

Thus the electronic conception of positive and negative valences not only indicates the nature of the radicals which, through the action of amines or water, lose carbon dioxide but it also affords a possible interpretation of the way in which the reactions proceed The theoretical deductions are based upon experimental facts and data afforded by the analogous action of pyridine upon chlorocarbonic ethylester It is quite conceivable that *the elimination of carbon dioxide from carbamino compounds of the proteins in physiological processes* may conform to the types of reactions just described

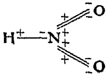
G Positive and Negative Nitro Groups: the Hydrolysis of Nitro Derivatives of Benzene.

In a compound of the general electronic formula $\mathrm{H}\overset{+\ \ -}{\text{——}}\mathrm{X}$, the atom or radical X is negative, but in $\mathrm{H}\overset{+\ \ -}{\text{——}}\mathrm{O}\overset{-\ \ +}{\text{——}}\mathrm{X}$ it is positive For instance, in nitrous acid, $\overset{+}{\mathrm{H}}\ \overset{-}{\mathrm{NO}_2}$, the nitro group is negative, but in nitric acid, $\overset{-}{\mathrm{HO}}\ \overset{+}{\mathrm{NO}_2}$, it is positive

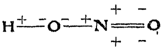
It is generally conceded that nitrous acid may exist in two tautomeric forms, presumably in equilibrium .—

$$\underset{\mathrm{I}}{\mathrm{H\ NO_2}} \rightleftharpoons \underset{\mathrm{II}}{\mathrm{H\ ONO}}$$

The electronic formulæ of tautomers I and II follow .—

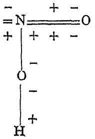


I



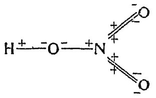
II

In formula I. the nitrogen atom possesses one negative and four positive units of valence, the algebraical sum of which is *three positive units* If the hydrogen atom is transferred from the nitrogen to the oxygen atom through the opening up of one of the double bonds between nitrogen and oxygen, the following intermediate structure may result —



It is assumed that polarization of the free positive and free negative unit of valence leaves the nitrogen atom in resultant tautomer II. with three positive units. Thus, it is evident that in each of the tautomers, I. and II., the nitrogen atom possesses algebraically three positive units of valence, and this marks the state of oxidation of the nitrogen atom in nitrous acid and the nitrites. In either tautomeric form the NO_2 or ONO radical functions negatively.

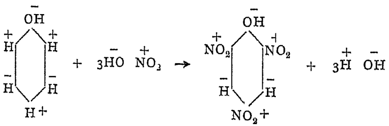
On the other hand, in nitric acid and the nitrates the nitrogen atom is in the state of oxidation represented by *five positive units* of valence as indicated in the formula—



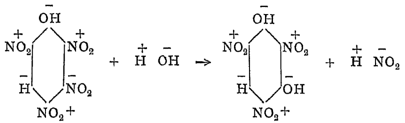
Here the NO_2 radical functions positively.

It may now be shown that the benzene nucleus may embody both positive and negative nitro groups, and that the latter, in hydrolytic reactions, yield nitrous acid or nitrites.

Phenol, when directly nitrated, yields ortho- and para-nitrophenol. Further nitration yields the two isomeric 1, 2, 4- and 1, 2, 6-dinitrophenols. Finally, nitration of either of these products gives the symmetrical trinitro derivative, picric acid. These reactions are summarized in the following electronic equation.—

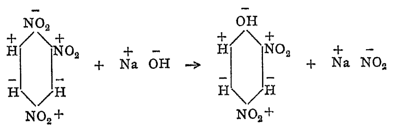


In trinitrophenol each of the nitro groups is positive, but the electronic formula indicates that in tetranitrophenol a fourth nitro group in position 3 or 5 would be negative. Now if some nitro groups are positive and others are negative there should be some marked difference in their behaviour toward certain reagents. These conclusions are substantiated by the fact that, as stated by J. B. Cohen,[55] "the nitro group in nitrobenzene is extremely stable compared with the fourth nitro group in tetranitrophenol, which water will remove in the form of nitrous acid" These facts are in perfect agreement with the electronic formula of tetranitrophenol, the hydrolysis of which yields nitrous acid ($\overset{+}{H}\ \overset{-}{NO_2}$ or $\overset{+}{H}\ \overset{-}{ONO}$) according to the electronic equation —

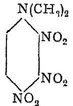


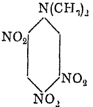
Since direct nitration with nitric acid results in the substitution of positive nitro groups, and since in tetranitrophenol the negative nitro group may occupy either of the equivalent positions 3 or 5, with negative hydroxyl in position 1, it follows that substituents in positions 1, 3, and 5 are negative while those in positions 2, 4, and 6 are positive This is a confirmation of the electronic formula of benzene and the substitution rule

It has been shown that halogen and carboxyl radicals may function either positively or negatively, depending principally upon the relative positions they may occupy in the benzene nucleus Direct evidence that when nitro groups occupy positions ortho or para to each other, one of them functions positively while the other functions negatively is shown by the replacement of only one of the nitro groups by negative hydroxyl or oxymethyl on interaction with $\overset{+}{Na}\ \overset{-}{OH}$ or $\overset{+}{Na}\ \overset{-}{OCH_3}$ and the concomitant formation of $\overset{+}{Na}\ \overset{-}{NO_2}$ For example, 1, 2-dinitro- and 1, 2, 4-trinitrobenzenes interact readily with solutions of sodium hydroxide or sodium methylate The nitro group in position 1 is replaced by $\overset{-}{OH}$ or $\overset{-}{OCH_3}$, and $\overset{+}{Na}\ \overset{-}{NO_2}$ is formed These reactions find an interpretation in the electronic formula of benzene and may be summarized in the following equation —

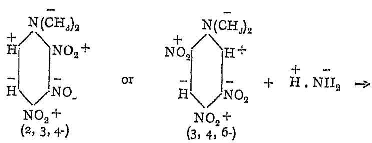


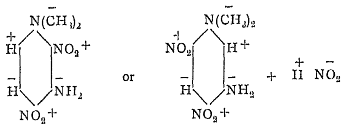
Other facts which not only indicate the existence of negative nitro groups but also further substantiate the electronic formula of benzene are recorded in the recent work of P van Romburgh and I W Wensink[56] who found that the nitro group in position 3 of either 2, 3, 4- or 3, 4, 6-trinitrodimethylaniline is readily replaced either by an NH_2—or $NH(CH_3)$—


(2, 3, 4-)


(3, 4, 6-)

group on interaction with alcoholic solutions of ammonia or methylamine, respectively Ordinarily, the hydrogen atoms of ammonia are positive and the three valences of the nitrogen atom are negative Hence the abbreviated electronic formulæ of ammonia and methylamine are $\overset{+}{H}\,.\,\overset{-}{NH_2}$ and $\overset{+}{CH_3}\ \overset{-}{NH_2}$ Accordingly, the replacement of only one of the three nitro groups (that in position 3) by $\overset{-}{NH_2}$ is perfectly analogous to the replacement of $\overset{-}{NO_2}$ by $\overset{-}{OH}$ in the reactions given above Furthermore, the nitro groups in positions 2 and 4 in the 2, 3, 4-compound are regarded as positive since they are not replaceable by $\overset{-}{NH_2}$ They also occupy positions ortho to the replacable negative nitro group of position 3 Again, in the 2, 4, 6-compound the nitro groups in positions 4 and 6 are also regarded as positive since they are not replaced by $\overset{-}{NH_2}$ They occupy positions ortho- and para-, respectively, to the negative nitro group of position 3 All of these facts and conclusions are embodied in and interpreted by the following electronic formulæ and equations —





In all benzene formulæ positions 2 and 6 are equivalent as are also positions 3 and 5 Accordingly, the 2, 3, 4- and 3, 4, 6-trinitrodimethylanilines (and their products of interaction with ammonia) coincidentally show that when the substituents in positions 1, 3, and 5 are negative, the substituents in positions 2, 4, and 6 are positive This also constitutes a further substantiation both of the electronic formula of benzene and the substitution rule

Additional evidence leading to the above conclusion might be described in detail but brief mention may suffice Recently Michele Giua [57] and A Contardi [58] have described a number of polynitro derivatives of benzene which suffer replacement of a nitro group by OH, O(CH_3), NH_2, and NH(CH_3) with the liberation of nitrites In some instances hydrolysis with water yields nitrous acid anhydride In these various instances two nitro groups are adjacent, i e, occupy positions ortho to each other, and only one of them suffers replacement Giua maintains that this behaviour substantiates the rule on the reactivity of the nitro groups in the benzene ring proposed by Korner and Laubenheimer who attribute the facility of reaction of the one nitro group to the adjacence of the two nitro groups and the consequent "*loosening*" action of one group upon the other This interpretation is not only vague but it fails to take into account the highly significant facts that the nitro group is replaced by a substituent of *negative polarity*, and that the group thus replaced is liberated as a *nitrite* in which *the nitro radical is also negative.* The electronic conception of positive and negative valences and the existence of positive and negative nitro groups affords a more satisfactory interpretation, since all of the facts noted are indicated and correlated by the electronic formula of benzene and the substitution rule Conversely, *the facts verify the electronic formula of benzene and the substitution rule*

In concluding this chapter, it may be remarked that the electronic conception of positive and negative valences and the electronic formula of benzene afford explanations of many anomalous properties and reactions which are generally classed as stereochemical problems The possibility of interpreting some of these properties and reactions indicates that they are not necessarily anomalous or irregular Hence it is hoped that a further extension of the principles and methods herewith presented may lead to the interpretation and solution of other problems

CHAPTER IX.

AN INTERPRETATION OF THE BROWN AND GIBSON RULE.

No single subject in the history of modern chemistry has received more attention than that of substitution in the benzene nucleus Concerning the introduction of two and three substituents, the foremost authority, A F. Holleman,[59] states that he has found 1300 memoirs, and, if we include the formation of other poly-substituted derivatives, this number is increased to 2000. Many rules and hypotheses have been proposed to correlate and explain these substitution reactions The foremost are those of Hubner,[60] Noelting,[61] Armstrong,[62] Brown and Gibson,[63] Collie,[64] Lapworth,[65] Blanksma,[66] Flurscheim,[67] Obermiller,[68] and Tschitschibabin [69]

A comprehensive review of the rules and hypotheses of most of the foregoing investigations is given by Holleman in his work, *Die direkte Einfuhrung von Substituenten in den Benzolkern* (1910), and in his lecture before the Société Chimique de France (1911) entitled *Sur les règles de substitution dans le noyau benzénique* Despite the immense amount of work accomplished in this field, Holleman states that no rule or theory has as yet furnished a satisfactory explanation of substitution in the benzene nucleus. "The question of knowing the reason why such or such group directs a new substituent chiefly to the para-, ortho-positions or chiefly to the meta-position, is not yet solved."

Of all the rules that have been proposed for determining whether a given benzene monoderivative shall give a meta-di-derivative or a mixture of ortho- and para-di-derivatives, that of Professor A Crum Brown and Dr John Gibson [70] is pre-eminent Quotations from their original article will describe their rule

A. The Brown and Gibson Rule.

"When a monobenzene derivative C_6H_5X is so treated as to give a dibenzene derivative C_6H_4XY, it is well known that, as a rule, this dibenzene derivative is either (*a*) exclusively, or nearly so, a *meta*-compound, or (*b*) a mixture of *ortho*- and *para*- with none or very little *meta*-, and that whether the case shall fall under (*a*) or (*b*) depends on the nature of the radical X, and not at all, or only very slightly, on the nature of Y.

"We have gone over all cases known to us, and have formulated a rule which holds in all these cases, and is always capable of rigorous application, so that, if in any case it should be found to fail, no excuse could be found for it. We shall best explain our rule by showing how we apply it. We shall write in column A a number of benzene mono-derivatives, in column B the radicles replacing one H of C_6H_6, in column C the hydrogen compounds of these radicles, in column D the hydroxycompounds of the same radicles, and in column E the letters *m* or *o-p* according as the mono-derivatives give *meta*- or a mixture of *ortho*- and *para*- di-derivatives.

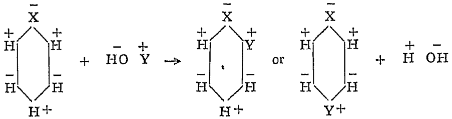
A	B	C	D.	E
C_6H_5Cl	Cl	HCl *	$HOCl$	*o-p*
C_6H_5Br	Br	HBr *	$HOBr$	*o p*
$C_6H_5CH_3$	CH_3	HCH_3 *	$HOCH_3$	*o p*
$C_6H_5NH_2$	NH_2	HNH_2 *	$HONH_2$	*o-p*
C_6H_5OH	OH	HOH *	$HO\ OH$	*o p.*
$C_6H_5NO_2$	NO_2	HNO_2	$HO.NO_2$ *	*m*
$C_6H_5CCl_3$	CCl_3	$HCCl_3$ *	$HO\ CCl_3$	*o-p*
$C_6H_5CO\ H$	$.CO\ H$	$HCO\ H$	$HO\ CO\ H$ *	*m*
$C_6H_5CO\ OH$	$CO\ OH$	$H\ CO\ OH$	$HO\ CO\ OH$ *	*m*
$C_6H_5SO_2\ OH$	$SO_2\ OH$	$HSO_2\ OH$	$HO\ SO_2\ OH$ *	*m*
$C_6H_5CO\ CH_3$	$CO\ CH_3$	$HCO\ CH_3$	$HO\ CO\ CH_3$ *	*m*
$C_6H_5CH_2.CO.OH$	$CH_2.CO\ OH$	$H\ CH_2\ CO.OH$ *	$HO.CH_2\ CO.OH$	*o-p.*

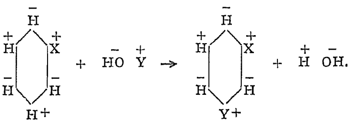
"In column C, we mark with an asterisk those substances which are *not* capable, by direct oxidation, of being converted into the corresponding hydrogen compounds in the next column, and in column D we mark with an asterisk those substances which can be formed by direct oxidation from the corresponding hydrogen compounds so that in each horizontal line there is one asterisk and one only, either in column C or in column D. By direct oxidation we mean oxidation by one step. Thus, no doubt $H\ CH_3$ can be converted into $HO.CH_3$, but not by one step of oxidation, whereas $H.CO\ CH_3$ can by one step of oxidation be converted into $HO.CO\ CH_3$. Now it will be seen that wherever the H compound is asterisked, we find *o-p* in column E, and whenever the HO compound is asterisked, we find *m* in column E. In other words, when X is naturally to be regarded as a derivative of HX, C_6H_5X gives *ortho-* and *para-* di-derivatives, and when X is naturally to be regarded as a derivative of HOX, C_6H_5X gives *meta-* di-derivatives Our test by which we determine whether X is to be regarded as derived from HX or HOX is, can HX be directly, by a single oxidizing step, be converted into HOX or not? If it cannot, then X is to be looked on as derived from HX, if it can, then X is to be looked on as derived from HOX"

Consider now the nitration of chlorobenzene and the chlorination of nitrobenzene in terms of the Brown and Gibson Rule According to this rule C_6H_5Cl is looked upon as a derivative of H Cl which is not directly oxidizable to HO Cl Therefore C_6H_5Cl yields ortho- and para- chloronitrobenzene on nitration On the other hand, $C_6H_5NO_2$ is regarded as a derivative of H NO_2 which is directly oxidizable to HO NO_2 Therefore, $C_6H_5NO_2$ yields meta-chloronitrobenzene on chlorination Thus the experimental facts and rule are correlated What is the underlying cause of this agreement between rule and fact? Brown and Gibson state that their rule is not a *law*, "because it has no visible relation to any mechanism by which the substitution is carried out in one way rather than in another way, but, if it is found to be rigorously applicable it must be related in some way to a law, and may be of use, both as grouping phenomena together and in guiding us to the cause of the formation of meta-compounds in certain cases and of ortho- and para- in others".

The electronic conception of valence and the electronic formula of benzene enable us to show that there is an underlying cause, a mechanism, so to speak, by which "substitution is carried out in one way rather than in another way," or, in other words, why some substitution reactions conform to the ortho-, para- type while others proceed according to the meta-type Both the reason and the mechanism become apparent when we determine the difference between X in HX, and X in HOX In our ordinary structural formulæ no difference is apparent, but from the electronic point of view, when H is positive and O is negatively bivalent, it necessarily follows that X in HX functions *negatively* while X in HOX functions *positively* as is evident in the electronic formulæ $\overset{+}{H}\text{——}\overset{-}{X}$ and

$\text{H}\overset{+\quad-}{\text{——}}\text{O}\overset{-\quad+}{\text{——}}\text{X}$ Accordingly, a mono-substituted derivative may be either $\overset{+}{C_6H_5}\ \overset{-}{X}$, if it is regarded as a derivative of $\overset{+}{H}\ \overset{-}{X}$, or $\overset{-}{C_6H_5}.\overset{+}{X}$, if it is looked upon as a derivative of $\overset{-}{HO}\ \overset{+}{X}$. Therefore (1) when X in C_6H_5X is *negative* and the entering substituent Y is *positive*, then *ortho-* and *para*-di-derivatives result. On the other hand (2) when X in C_6H_5X is *positive* and the entering substituent Y is *positive*, then *meta*-di-derivatives are formed. These principles are embodied in the following typical equations —

(1)


(2)


Thus, the electronic formula of benzene is correlated with the electronic interpretation of the Brown and Gibson rule, thereby showing a visible relation to a mechanism by which substitution is carried out in one way rather than in another way. Section A of the preceding Chapter VIII. presents concrete examples of the above scheme in the nitration of chlorobenzene, $\overset{+}{C_6H_5}\overset{-}{Cl}$, and in the chlorination of nitrobenzene, $\overset{-}{C_6H_5}\overset{+}{NO_2}$. The electronic formulæ of the products of these interactions, namely, ortho- and para- and meta-chloronitrobenzene, are correlated not only with the methods of their preparation and their chemical properties, but also with the Brown and Gibson rule.

In many substitution reactions, ortho-, para-, and meta-di-substituted derivatives of benzene are formed *simultaneously*. An interpretation of these simultaneous reactions necessitates a further development of the principle of electronic tautomerism which will be presented after a further analysis of the Brown and Gibson rule has been considered.

B. A Further Analysis of the Brown and Gibson Rule.

In presenting a further analysis of the Brown and Gibson rule it is necessary, first, to bring out more fully the hidden significance of the difference between compounds of the type HX which are not directly oxidizable to HOX and those which are directly oxidizable to HOX

Some writers have taken exception to this point of view which Brown and Gibson assumed as their basis of classifying substituents For instance, Holleman[71] states that the rule "although remarkable and representing very well many of the observed facts, does not give satisfaction since it depends entirely upon the question of the direct oxidation of the hydrogen compounds of the substituents Thus, at the time (1892) when Brown and Gibson published their rule, methane, H CH_3, could not be oxidized directly to methyl alcohol, HO. CH_3, hence, according to the rule, the radical CH_3 should direct the entering substituent to the ortho and para positions But since the time of the publication of the rule, Bone has proved that the primary oxidation product of methane during combustion is methyl alcohol As a consequence, the radical CH_3 should then direct the entering substituent to the meta position This discovery of Bone renders the rule inexact. While it is perfectly true that one cannot directly transform H Cl to HO Cl, yet on the other hand no one is certain that this will always be impossible" Therefore, Holleman contends that with the progress of science the Brown and Gibson rule becomes less and less applicable

Now this criticism of Holleman is only apparently justified, because Brown and Gibson unfortunately based their classification of substituents upon the debatable standpoint of the direct oxidizability in one step of HX to HOX It has been shown that the chief point of distinction between the two classes of substituents is not the direct oxidizability of HX to HOX but depends rather upon the electronic interpretation of the rule in conjunction with the electronic formula of benzene, and the fact that X in HX is negative while X in HOX is positive. These points of view invalidate Holleman's criticism of the Brown and Gibson rule

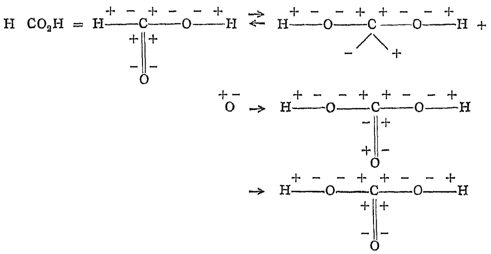
Further light may be thrown upon the nature of the substituents (X) commonly found in the benzene nucleus by considering the behaviour of certain HOX compounds as oxidizing agents, and the susceptibility to oxidation of certain HX compounds, thus placing the Brown and Gibson classification on a different basis Consider, first, a few of those substituents (OH, NH_2, Cl, and CH_3), which Brown and Gibson regarded as naturally derived from HX, not directly oxidizable to HOX It is particularly noteworthy that the hydroxyl compounds of each of these substituents may function as an oxidizing agent, while their hydrogen compounds are not oxidizing agents in the common sense of the word Furthermore, the hydroxyl compounds of these substituents are less stable than their corresponding hydrogen compounds When HOX functions as an oxidizing agent ($HOX \rightarrow HX + O$), yielding HX and oxygen (either free or combined) there is a change in the polarity of X from $\overset{+}{X}$ to $\overset{-}{X}$ This change may be represented as involving either an oxidation of negative hydroxyl ions by positive chlorine ions ($HO\ \ Cl = \overset{-}{HO} + \overset{+}{Cl} \rightarrow \overset{+}{H} + \overset{-}{Cl} + O$) or an intramolecular oxidation and reduction ($\mathrm{H}\overset{+\ \ -}{\text{———}}\mathrm{O}\overset{-\ \ +}{\text{———}}\mathrm{X} \rightarrow \mathrm{H}\overset{+\ \ -}{\text{———}}\mathrm{O}\overset{+\ \ -}{\text{———}}\mathrm{X} \rightarrow \mathrm{H}\overset{+\ \ -\ \ -}{\text{———}}\mathrm{X} + \overset{+}{\mathrm{O}}$) Now, since compounds of the type HOX are less stable than those of the type HX, as shown by oxidation reactions, and since these oxidations involve the transition from $\overset{+}{X}$ to $\overset{-}{X}$, we may accordingly assume that $\overset{-}{X}$ is more stable than $\overset{+}{X}$ In other words, the tendency for X to function negatively is more pronounced than its tendency to function positively, but it may function either way as its $\overset{+}{H}\ \overset{-}{X}$ and $\overset{-}{HO}\ \overset{+}{X}$ compounds show This may be postulated as a general property of those substituents which Brown and Gibson regarded as naturally derived from HX not directly oxidizable to HOX

In order to complete the analysis of the Brown and Gibson rule it will be necessary to consider from the same points of view a few of those substituents, namely, CO_2H, COH, SO_3H

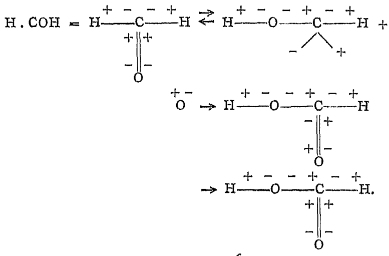
and NO_2, which were formerly regarded as belonging to the type HOX derivable by direct oxidation of HX. In fact, each of these HX compounds may be oxidized directly to the corresponding HOX compound, but it should be noted that X is a complex radical and the oxidation involves fundamental changes both in the number and polarity of the valences of certain atoms comprising these radicals. These features may be illustrated by the electronic equations for the oxidations in which oxygen as $\overset{+\,-}{\text{O}}$ functions as the oxidizing agent through the acquisition of electrons and the consequent conversion of certain negative valences in the radical X to positive valences—

$$\overset{+\,-}{\text{O}} \rightarrow \overset{-\,-}{\text{O}} + 2\oplus,\ \overset{-}{\text{X}} + 2\oplus \rightarrow \overset{+}{\text{X}}$$

The complete electronic equations for the oxidation of (1) formic acid, (2) formaldehyde, (3) sulphurous acid, and (4) nitrous acid are as follows —

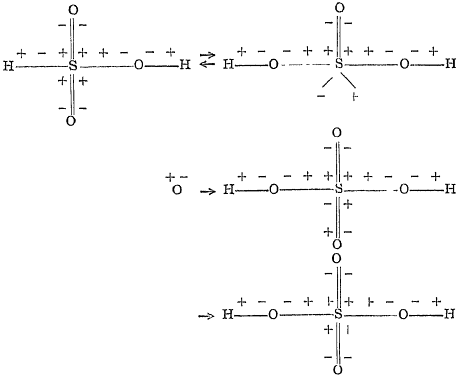
(1)


$$\text{H CO}_2\text{H} = \text{H}\overset{+\ \ -}{\text{—}}\underset{\substack{+\|+\\ -\|-\\ \text{O}}}{\text{C}}\overset{+\ \ -}{\text{—}}\text{O}\overset{-\ \ +}{\text{—}}\text{H} \rightleftarrows \text{H}\overset{+\ \ -}{\text{—}}\text{O}\overset{-\ \ +}{\text{—}}\underset{-\diagup\diagdown+}{\text{C}}\overset{+\ \ -}{\text{—}}\text{O}\overset{-\ \ +}{\text{—}}\text{H} + \overset{+\,-}{\text{O}} \rightarrow \text{H}\overset{+\ \ -}{\text{—}}\text{O}\overset{-\ \ +}{\text{—}}\underset{\substack{-\|+\\ +\|-\\ \text{O}}}{\text{C}}\overset{+\ \ -}{\text{—}}\text{O}\overset{-\ \ +}{\text{—}}\text{H} \rightarrow \text{H}\overset{+\ \ -}{\text{—}}\text{O}\overset{-\ \ +}{\text{—}}\underset{\substack{+\|+\\ -\|-\\ \text{O}}}{\text{C}}\overset{+\ \ -}{\text{—}}\text{O}\overset{-\ \ +}{\text{—}}\text{H}$$

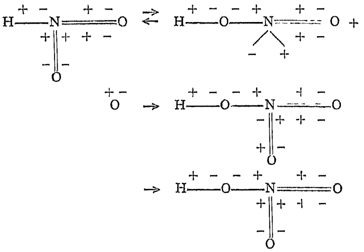
(2)


$$\text{H.COH} = \text{H}\overset{+\ \ -}{\text{—}}\underset{\substack{+\|+\\ -\|-\\ \text{O}}}{\text{C}}\overset{-\ \ +}{\text{—}}\text{H} \rightleftarrows \text{H}\overset{+\ \ -}{\text{—}}\text{O}\overset{-\ \ +}{\text{—}}\underset{-\diagup\diagdown+}{\text{C}}\overset{-\ \ +}{\text{—}}\text{H} + \overset{+\,-}{\text{O}} \rightarrow \text{H}\overset{+\ \ -}{\text{—}}\text{O}\overset{-\ \ +}{\text{—}}\underset{\substack{-\|+\\ +\|-\\ \text{O}}}{\text{C}}\overset{-\ \ +}{\text{—}}\text{H} \rightarrow \text{H}\overset{+\ \ -}{\text{—}}\text{O}\overset{-\ \ +}{\text{—}}\underset{\substack{+\|+\\ -\|-\\ \text{O}}}{\text{C}}\overset{-\ \ +}{\text{—}}\text{H}.$$

(3) $H.SO_3H$ =



(4) $H.NO_2$ =



The above oxidations proceed readily, in fact most of the compounds are oxidized directly by atmospheric oxygen, ($O_2 = \overset{+\ \ -}{\underset{-\ \ +}{O\!=\!=\!O}} \rightarrow 2\overset{+-}{O}$) The tendency for the acid HX to change to HOX involves a change in the polarity of the complex radical X from $\overset{-}{X}$ to $\overset{+}{X}$, and accordingly $\overset{+}{X}$ may be regarded as more stable than $\overset{-}{X}$ In other words, the tendency for X to function positively ($\overset{-}{HO}\ \overset{+}{X}$) is more pronounced than its tendency to function negatively $(\overset{+}{H}\ \overset{-}{X})$, but it may function either way as the hydrogen and hydroxyl compounds show. The above may be postulated as a general property of those substituents which Brown and Gibson regarded as naturally derived from HOX which results from the direct oxidation of HX

Other points of significance may be noted in Equations 1-4 above In formic acid, equation 1, three of the carbon valences are positive while the fourth is negative. In carbonic acid, four carbon valences are positive. Prior to the action of $\overset{+-}{O}$, formic acid is in equilibrium with a tautomeric modification in which the carbon atom is bivalent and shows one free positive and one free negative valence. These free valences unite with $\overset{+-}{O}$ and, either simultaneously or subsequently, the negative carbon valence is oxidized to a positive valence and oxygen $(\overset{+-}{O})$ thereby becomes negatively bivalent $(\overset{--}{O})$ The tautomeric modification of formic acid, showing a free positive and a free negative valence, would through the polarization of these valences present an illustration of a bivalent carbon compound

In this connection it should be noted that Stieglitz[72] has given a detailed account of the oxidation of carbon compounds, in particular formaldehyde, showing by means of the chemometer that there is involved an actual transfer of electrical charges The classification of sulphurous and nitrous acids with formaldehyde in the present discussion leads to the suggestion that certain sulphites and nitrites might lend themselves to similar significant demonstrations

In Equation 3 note that sulphurous acid (H SO_3H) is ordinarily written (HO . SO_2H), in which the sulphur atom (comparable to the carbon atom above) shows a free positive and a free negative valence, and the polarization of these valences renders sulphur quadrivalent, but, on oxidation to sulphuric acid, the sulphur atom becomes sexavalent. In precisely the same manner nitrous acid (H NO_2) is commonly written (HO NO) in which nitrogen is tervalent, but oxidation to nitric acid renders nitrogen quinquevalent. Now Equations 1-4 show that formaldehyde, formic acid, sulphurous acid, and nitrous acid belong to the same class and same type of oxidizable compounds Since the sulphur atom in sulphurous acid increases its valence by two on oxidation to sulphuric acid, and since the nitrogen atom in nitrous acid likewise increases its valence by two when oxidized to nitric acid, it follows, similarly, that the carbon atom in formaldehyde and formic acid must undergo likewise an increase of two in its valence when the compounds are oxidized to formic acid and carbonic acid, respectively In other words, this classification of the substituents and the electronic system of oxidation lends further support to, and an electronic interpretation of, the existence of bivalent carbon compounds.

The extended interpretation and analysis of the Brown and Gibson rule brings out the following facts —

1 Certain substituents (OH, Cl, Br, I, NH_2, CH_3, etc) lead to the formation chiefly of ortho- and para-derivatives of benzene, because their tendency to function negatively is more pronounced than their tendency to function positively This tendency may be formulated thus $\overset{-}{X} > \overset{+}{X}$.

2 Certain other substituents (CO_2H, COH, SO_3H, NO_2, etc) lead to the formation chiefly of meta-derivatives of benzene, because their tendency to function positively is more pronounced than their tendency to function negatively. This tendency may be formulated thus $\overset{+}{X} > \overset{-}{X}$.

3 The objections which have been directed against the Brown and Gibson rule have been based upon the question of the direct oxidizability of HX to HOX. These objections are invalid, because the distinction between the two classes of substituents rests upon the facts summarized in paragraphs (1) and (2) above, and the fact that X in HX is negative while X in HOX is positive *These distinctions, in conjunction with the electronic formula of benzene, show why certain mono-substituted derivatives of benzene yield chiefly ortho- and para-di-substituted derivatives, while others yield chiefly meta-di-substituted derivatives.*

CHAPTER X

ELECTRONIC TAUTOMERISM OF BENZENE DERIVATIVES

IN Section D of Chapter II. and in Section C of Chapter III the conception of *electronic tautomerism* was developed. The purpose of the present chapter is to consider a number of experimental facts and to show that their interpretation not only fully warrants but also demands the assumption of the existence of electromers in dynamic equilibrium, i.e., electronic tautomerism. This conception was first proposed by the author in 1908. The following words[73] embody the definition:—

"The hypothesis of positive and negative valences suggests the possibility of there being at least two distinct types or electromers of a binary compound. Hence two mono-substituted derivatives of benzene, $\mathrm{C_6H_5}\overset{+\ \ -}{\text{——}}\mathrm{X}$ and $\mathrm{C_6H_5}\overset{-\ \ +}{\text{——}}\mathrm{X}$, should be possible while only one is known. Therefore, if both electromers exist and only one substance is identified, it follows that the electromers are either not distinguishable by (present) physical methods, or that one electromer is transformable into the other through the transposition of electrons:—

$$\mathrm{C_6H_5}\overset{+\ \ -}{\text{——}}\mathrm{X} \rightleftharpoons \mathrm{C_6H_5X} \rightleftharpoons \mathrm{C_6H_5}\overset{-\ \ +}{\text{——}}\mathrm{X}\text{"}$$

A study of various hydrolytic reactions compels one to assume the existence of such electromers. As previously noted, when a compound, XY, on hydrolysis yields HY and HOX, then the compound is represented by the formula $\overset{+}{\mathrm{X}}\ \overset{-}{\mathrm{Y}}$. The hydrolytic reaction conforms to the following scheme (*a*):—

$$(a)\ \overset{+}{\mathrm{X}}.\overset{-}{\mathrm{Y}} + \overset{+}{\mathrm{H}}\ \overset{-}{\mathrm{OH}} \rightarrow \overset{+}{\mathrm{H}}\ \overset{-}{\mathrm{Y}} + \overset{-}{\mathrm{HO}}.\overset{+}{\mathrm{X}}$$

If, on the other hand, the conditions of hydrolysis are such that compound XY yields HX and HOY, then XY must possess the formula $\overset{-}{\mathrm{X}}.\overset{+}{\mathrm{Y}}$. The hydrolysis conforms to the scheme (*b*):—

$$(b)\ \overset{-}{\mathrm{X}}.\overset{+}{\mathrm{Y}} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{OH}} \rightarrow \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{X}} + \overset{-}{\mathrm{HO}}.\overset{+}{\mathrm{Y}}.$$

Now it has been found that phenylsulphonic acid, $C_6H_5 . SO_3H$, on hydrolysis, in *alkaline solution* yields sulphurous acid $H\ SO_3H$, and phenol, $C_6H_5\ OH$ This reaction conforms to scheme (*a*) thus —

$$(a)\ \overset{+}{C_6H_5}\ \overset{-}{SO_3H} + \overset{+}{H} . \overset{-}{OH} \rightarrow \overset{+}{H}\ \overset{-}{SO_3H} + \overset{+}{C_6H_5}\ \overset{-}{OH}$$

On the other hand, the hydrolysis of the same compound, phenylsulphonic acid, in *acid solution* yields benzene, $H\ C_6H_5$, and sulphuric acid, $HO\ SO_3H$ This reaction conforms to scheme (*b*) thus —

$$(b)\ \overset{-}{C_6H_5} . \overset{+}{SO_3H} + \overset{+}{H}\ \overset{-}{OH} \rightarrow \overset{+}{H} . \overset{-}{C_6H_5} + \overset{-}{HO}\ \overset{+}{SO_3H}$$

These facts compel us to conclude that phenylsulphonic acid may enter into chemical reactions either as $\overset{+}{C_6H_5} . \overset{-}{SO_3H}$ or as $\overset{-}{C_6H_5}\ \overset{+}{SO_3H}$ From the tautomeric point of view, phenylsulphonic acid may be regarded as an equilibrium mixture of two *electronic isomers*, or *electromers*

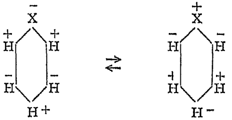
$$(\overset{+}{C_6H_5}\ \overset{-}{SO_3H} \rightleftharpoons \overset{-}{C_6H_5} . \overset{+}{SO_3H})$$

and any other mono- or poly-substituted derivative of benzene may be regarded similarly, as will be shown later

Consider any mono-substituted derivative of the general formula C_6H_5X which will now be regarded as

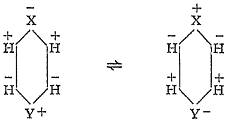
$$(\overset{+}{C_6H_5} . \overset{-}{X} \rightleftharpoons \overset{-}{C_6H_5}\ \overset{+}{X})$$

Indicating only the polarities of the hydrogen atoms of the nucleus, the equilibrium is represented thus —

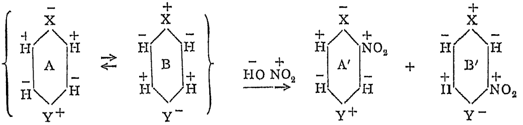


Note particularly that the change in the polarity of the substituent X involves simultaneously a change in the polarities of the hydrogen atoms, but that in each electromer those atoms (or substituents) ortho and para to X are opposite in sign to X, while those atoms (or substituents) meta to X are of the same sign as

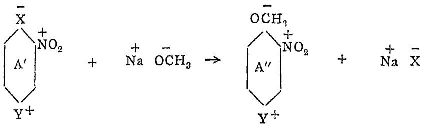
X This, of course, is the essential feature of all of the electronic formulæ of benzene, namely, that hydrogen atoms or substituents in positions 1, 3, and 5 of any given electromer are opposite in sign to the hydrogen atoms or substituents in positions 2, 4, and 6 of the same electromer, otherwise the symmetry, and consequently the stability, of the benzene nucleus could not be maintained A detailed mechanism of the transposition of electrons, the centric valences, etc., involved in the electronic tautomerism of benzene derivatives will be given later. For the present, the simpler formulæ involving only the hydrogen atoms and substituents are sufficient In a similar manner the electronic tautomerism of a di-substituted derivative of benzene, for example C_6H_4XY, in which X and Y are in para positions to each other, may be represented thus :—



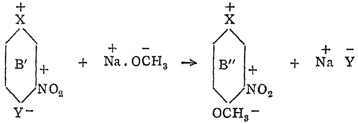
When two substituents occupy positions either ortho or para to each other they are of opposite polarity Hence in the electronic formula for a *p*-dihalogen benzene in which the halogen atoms X and Y are different chemically, it follows that if X is negative, Y is positive, or, if X is positive, Y is negative Now, in the nitration of a *p*-di-substituted derivative of benzene only two mono-nitro substitution products are possible, and, from the standpoint of the principle of electronic tautomerism as applied to a *p*-dihalogen benzene, the nitration reaction should conform to the following general scheme —



If the principles underlying this general scheme are correct, then certain definite consequences follow which should lend themselves to verification by experiment What are some of these consequences? If the electromers of C_6H_4XY (designated as A and B) are in tautomeric equilibrium and if each electromer interacts with nitric acid, the respective isomers A′ and B′, should be formed Note particularly that in the isomer A′, X is negative and Y is positive, while in isomer B′, X is positive and Y is negative In view of the facts previously presented, notably the action of sodium hydroxide or sodium methylate upon *o*-, *p*-, and *m*-chloronitrobenzenes, it follows that isomer A′ on interaction with sodium methylate ($\overset{+}{\text{Na}}\ \overset{-}{\text{OCH}_3}$) should exchange $\overset{-}{\text{X}}$ for $\overset{-}{\text{OCH}_3}$ and liberate $\overset{+}{\text{Na}}\ \overset{-}{\text{X}}$ according to equation (1) —

(1) 

On the other hand, isomer B′ should exchange $\overset{-}{\text{Y}}$ for $\overset{-}{\text{OCH}_3}$ and liberate $\overset{+}{\text{Na}}\ \overset{-}{\text{Y}}$ according to equation (2) —

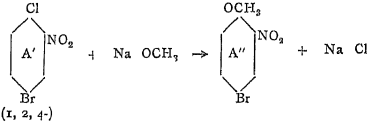
(2) 

Furthermore, if electromers A and B are in tautomeric equilibrium and nitration yields a mixture of isomers A′ and B′ then the action of sodium methylate upon this mixture should yield not only the oxymethyl derivatives, A″ and B″ (equations (1) and (2), respectively), but also *a mixture of the sodium halides,* $\overset{+}{Na}\ \overset{-}{X}$ *and* $\overset{+}{Na}\ \overset{-}{Y}$. An experimental verification of these predictions would lead to a very definite conclusion, namely, that *the para mixed dihalogen compound,* C_6H_4XY, *affords an example of electronic tautomerism* Otherwise it would be difficult, if not impossible, to account for the simultaneous formation of the mixed halides $\overset{+}{\text{Na}}\ \overset{-}{\text{X}}$ and $\overset{+}{\text{Na}}\ \overset{-}{\text{Y}}$ when sodium methylate interacts

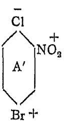
of the mixed dihalogen benzene.

Experimental facts will now be considered which are completely in agreement with the principles and general reactions just postulated. Holleman and Heincken[74] have made a thorough study of the nitration (at 0°) of various mixed dihalogen benzenes. For the present, attention will be confined to the nitration of *p*-chlorobromobenzene, which gave a mixture of the isomers 1, 2, 4- and 1, 3, 4-chloronitrobromobenzenes. In developing a quantitative chemical method for determining the yields of these isomers in the nitration mixture, Holleman found that the 1, 2, 4-isomer heated with 0.35 N sodium methylate solution in a sealed tube for five hours at 80° gave *practically complete displacement of chlorine as sodium chloride while the bromine remained intact.* The reaction proceeded quantitatively (98.40 per cent.) according to equation (3).—

(3)

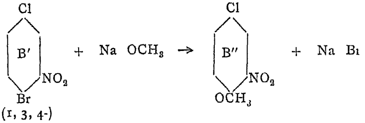


Note that this reaction is perfectly analogous to equation (1) given above, in which $\overset{-}{X}$ becomes $\overset{-}{Cl}$, and $\overset{+}{Y}$ becomes $\overset{+}{Br}$. The liberated sodium halide is $\overset{+}{Na}\ \overset{-}{Cl}$. In other words, the 1, 2, 4-isomer (A′) has the electronic formula

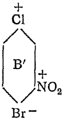


Otherwise the liberation of chlorine as $\overset{+}{Na}\ \overset{-}{Cl}$ is inexplicable.

On the other hand, the 1, 3, 4-isomer on interaction with sodium methylate (under identical conditions) suffered *practically complete displacement of bromine as sodium bromide while the chlorine atom remained intact.* The reaction proceeded quantitatively (98.00 per cent.) according to equation (4).

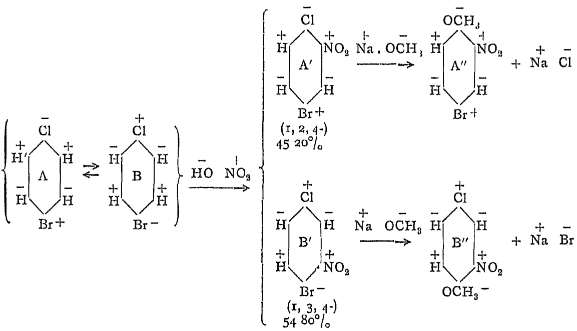
(4) 

Note that this reaction is perfectly analogous to equation (
above, in which $\overset{+}{X}$ becomes $\overset{+}{Cl}$, and $\overset{-}{Y}$ is $\overset{-}{Br}$. The liberate
sodium halide is $\overset{+}{Na}$ $\overset{-}{Br}$ In other words, the 1, 3, 4-isom
(B′) has the electronic formula



In no other way can the elimination of bromine as $\overset{+}{Na}$ $\overset{-}{Br}$ be e
plained

The quantitative interaction of 1, 2, 4- and 1, 3, 4-chlor
nitrobromobenzene with sodium methylate enabled Holleman
determine the relative quantities of these isomers obtained
nitrating *p*-chlorobromobenzene The sodium chloride a
sodium bromide liberated were precipitated as silver chloride a
silver bromide An analysis of the mixed precipitates gave t
percentage yields of the isomers calculated upon the ratios
AgCl 1, 2, 4-isomer, and AgBr 1, 3, 4-isomer These c
culations were based upon equations (3) and (4) which are perfect
analogous to the preceding electronic equations (1) and (2),
spectively The yields of the isomers were 45 20 per cent a
54 80 per cent respectively The complete correlation of all
these reactions with the electronic formulæ and the principle
electronic tautomerism is embodied in the following scheme —



Now a survey of the above scheme shows that those molecules of 1, 4-chlorobromobenzene which interact with nitric acid to give the 1, 2, 4-isomer, which in turn exchanges its *chlorine* atom for OCH_3 and yields *sodium chloride*, cannot be identical with the molecules of 1, 4-chlorobromobenzene which interact with nitric acid to give the 1, 3, 4-isomer, which in turn exchanges its *bromine* atom for OCH_3 and yields *sodium bromide* In other words, the 1, 2, 4-isomer (A′), containing $\overset{-}{\mathrm{Cl}}$ and $\overset{+}{\mathrm{Br}}$ must be derived from molecules of 1, 4-chlorobromobenzene which also contain $\overset{-}{\mathrm{Cl}}$ and $\overset{+}{\mathrm{Br}}$, i e, electromer A, and the 1, 3, 4-isomer (B′) containing $\overset{+}{\mathrm{Cl}}$ and $\overset{-}{\mathrm{Br}}$, must be derived from molecules of 1, 4-chlorobromobenzene which also contain $\overset{+}{\mathrm{Cl}}$ and $\overset{-}{\mathrm{Br}}$, i.e, electromer B. Thus *the existence of two types of molecules of* 1, 4-*chlorobromobenzene, namely, electromers* A *and* B, *is conclusively indicated Their simultaneous interaction with nitric acid clearly indicates tautomeric equilibrium* The relative yields of the isomers A′ and B′ are functions of the speeds of interaction of nitric acid with the respective electromers A and B, and, as will be shown in a subsequent chapter, the speeds of interaction are intimately related to the concentrations of the respective electromers in the reaction mixture.

It will not be necessary to extend this chapter by giving similarly detailed descriptions of the nitrations of other mixed dihalogen benzenes, such as *p*-fluorochloro-, *p*-fluorobromo-, *p*-chloroiodo-, *o*-chlorobromo-, *o*-chloroiodo-, and *o*-bromoiodo benzene Each example conforms perfectly to the schemes and principles just presented In conclusion, it is maintained that each of these cases further substantiates the principle of electronic tautomerism or the existence of electromers in dynamic equilibrium

Any objection to the use of the conception of electronic tautomerism on the grounds that electronic isomers (electromers) have not as yet been isolated is unwarranted because the conception of tautomerism, both in its historical and practical aspects, neither involves nor demands the immediate possibility of the isolation of the tautomers In 1885, Laar,[75] in a paper *Ueber die Moglichkeit mehrerer Strukturformeln fur dieselbe chemische Verbindung*, defined tautomerism as the phenomenon of one substance doing duty for two structural isomers, *but the isolation of dynamic isomers or desmotropes was not effected until* 1893, the earliest examples being acetyldibenzoylmethane, tribenzoylmethane, and mesityloxide-oxalic ester described by Claisen [76] Strictly speaking, the term *tautomeric* is now applied to substances in which *only the equilibrium mixture of the structural isomers is known*, the term *desmotropic* is employed in cases where the isomers have been shown to be capable of independent existence [77] The existence of electromers in dynamic equilibrium has been conclusively indicated Their isolation as *electronic desmotropes* has not as yet been effected. Further discussion of this phase of the subject is considered in Chapters XXIII and XXIV.

The phenomenon of electronic tautomerism is met repeatedly in the interpretations of substitution reactions in the benzene nucleus A number of these reactions is described in the following chapter

CHAPTER XI

THE SIMULTANEOUS FORMATION OF ORTHO-, PARA-, AND META-SUBSTITUTED DERIVATIVES OF BENZENE

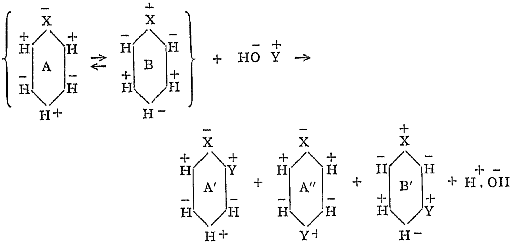
A. Formation of Isomeric Di-substituted Derivatives.

IN the electronic interpretation of the Brown and Gibson rule (Chapter IX.), the formations of ortho- and para-compounds on the one hand, and meta-compounds on the other, were regarded as distinct and separate processes because, as a general rule, a given mono-substituted compound yields chiefly a meta-di-derivative or a mixture of ortho- and para-di-derivatives In many substitution reactions isomeric ortho-, para-, and meta-di-substituted derivatives are formed simultaneously. The Brown and Gibson rule does not cover these cases. Consequently it becomes necessary to explain (A) the simultaneous formation of isomeric ortho-, para-, and meta-di-substituted derivatives, and also (B) the simultaneous formation of isomeric poly-substituted derivatives of benzene These explanations involve the electronic formula of benzene, the rule of substitution, *and the conception of electronic isomers or electromers in dynamic equilibrium, i e , electronic tautomerism*

It is necessary, first, to recall a well-established fact, namely, that in a mixture of two isomers ($A \rightleftharpoons B$) capable of changing one into the other with such readiness that the balance between them is rapidly restored, the addition of a given substance C will result in reaction either with A, or with B, or with both A and B. If interaction occurs between A and C, B will be transformed into A on account of the disturbance of the equilibrium The mixture then reacts as though it consisted wholly of A If C reacts only with B, the mixture behaves, for the same reason, as though B were the only substance present In some instances two simultaneous independent reactions may occur, namely, the interaction of A and C simultaneously with the interaction of B and C. In a precisely similar manner a given reagent, $\overset{-}{HO}.\overset{+}{Y}$, in the presence of a tautomeric mixture of electromers

$$(\overset{+}{C_6H_5}.\overset{-}{X} \rightleftharpoons \overset{-}{C_6H_5}\ \overset{+}{X})$$

may react with the one electromer or the other, or with both electromers. A complete scheme of interaction follows —



It should be observed that if $\overset{-}{HO}.\overset{+}{Y}$ reacts only with $\overset{+}{C_6H_5}\ \overset{-}{X}$ (electromer A) then only ortho- and para-di-substituted derivatives (A′ and A″) are formed. Such is the case when chlorobenzene is nitrated: the products of the interaction are ortho- and para-chloronitrobenzene. If $\overset{-}{HO}.\overset{+}{Y}$ reacts only with $\overset{-}{C_6H_5}\ \overset{+}{X}$ (electromer B), then only a meta-di-substituted derivative (B′) results. Such is the case when nitrobenzene is chlorinated: the product of the reaction is meta-chloronitrobenzene. If $\overset{-}{HO}\ \overset{+}{Y}$ interacts simultaneously with both electromers (A and B) then ortho-, meta-, and para-di-substituted derivatives (A′, B′, and A″, respectively) will be formed. The possibility and the extent of these reactions (as in all reactions with tautomeric substances) are dependent upon several conditions such as the solvent medium, catalytic agent, temperature, concentration of the electromers, the speed of transition of one electromer into the other, and the respective speeds of interaction of the substituting agent with the respective electromers. These conditions are the problems which confront us in all research involving tautomers, and likewise will be met in the case of electronic tautomers.

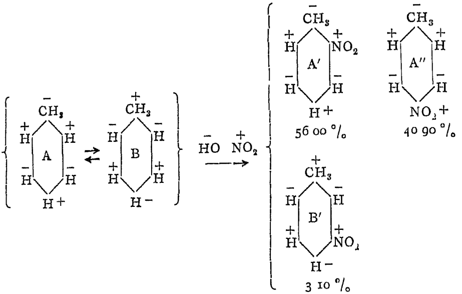
Having given a general scheme for the simultaneous formation of ortho-, meta-, and para-di-substituted derivatives, one of the many examples which are in accord with and, therefore, confirm the scheme, should now be considered. For instance, in the nitration of toluene, the substituent (X) already present in the nucleus is the methyl radical which may function either positively or negatively; but in Section B of Chapter IX. it has been shown that its tendency to function negatively is more pronounced than its tendency to function positively, i.e., $\overset{-}{CH_3} > \overset{+}{CH_3}$. Hence, in the tautomeric equilibrium—

$$\overset{+}{C_6H_5} . \overset{-}{CH_3} \rightleftharpoons \overset{-}{C_6H_5}\ \overset{+}{CH_3},$$

the former electromer would predominate and interaction with $\overset{-}{HO} . \overset{+}{NO_2}$ would lead to a greater yield of *o*- and *p*-nitrotoluenes than of *m*-nitrotoluene. The predominance or preponderance of the electromer $\overset{+}{C_6H_5}\ \overset{-}{CH_3}$ over the electronic tautomer $\overset{-}{C_6H_5} . \overset{+}{CH_3}$ may be correlated with the speeds of reaction with nitric acid; i.e., if the former electromer reacts more rapidly than does the latter electromer, then the yield of ortho- and para-nitrotoluenes would exceed that of meta-nitrotoluenes.

The predominance of one electromer over the other may be regarded as equivalent to a greater concentration of the one electromer. Since concentration is a principal factor of the velocity of reaction, it is evident that a direct relationship exists between the predominance or preponderance of a given electromer and the velocity of the substitution reaction in which it is engaged.

The foregoing assumptions are confirmed by experimental facts, since toluene when nitrated yields 56.00 per cent. of the *o*-, 40.90 per cent. of the *p*-, and 3.10 per cent. of the *m*-nitrotoluene. The simultaneous formation of the three isomers is indicated in the following scheme:—



Here electromer A predominates, i e, its speed of interaction with nitric acid is greater than the speed of interaction of electromer B with nitric acid

Consider now, on the other hand, the nitration of benzoic acid The substituent (X) already present in the nucleus is CO_2H, which may function either positively or negatively, but $\overset{+}{CO_2}H > \overset{-}{CO_2}H$, i e, the tendency for the carboxyl radical to function positively is more pronounced than is its tendency to function negatively Accordingly, in the equilibrium—

$$\overset{+}{C_6H_5}\ \overset{-}{CO_2H} \rightleftharpoons \overset{-}{C_6H_5}\ \overset{+}{CO_2H},$$

the latter electromer (in which the carboxyl radical is positive) would predominate, and if its speed of interaction with $\overset{-}{HO}\ \overset{+}{NO_2}$ is greater than the speed of interaction between $\overset{+}{C_6H_5} . \overset{-}{CO_2H}$ and $\overset{-}{HO} . \overset{+}{NO_2}$, then the yield of *m*-nitrobenzoic acid should exceed that of the combined yields of the ortho- and para-compounds These assumptions are confirmed by the facts, since benzoic acid on nitration yields 80 30 per cent. of the meta-compound, 18 50 per cent. of the ortho, and 1 20 per cent of the *p*-nitrobenzoic acid The electronic equations conform to the general scheme given above (p 94)

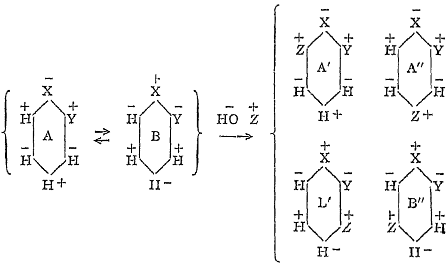
Many other examples of the simultaneous formation of ortho-, meta-, and para-di-substituted derivatives of benzene might be presented in detail. They are in complete agreement with, and accordingly confirm, the principle of the electronic tautomerism of the electromers of the benzene derivatives, the general rule for substitution, and the scheme for the simultaneous formation of ortho-, meta-, and para-di-substituted derivatives of benzene.

B. Formation of Isomeric Poly-substituted Derivatives.

The principles underlying the simultaneous formation of poly-substituted derivatives of benzene are identical with those just given in the preceding section (A) and may be illustrated by considering the introduction of a third substituent (Z) into (1) an ortho-, (2) a para-, and (3) a meta-di-substituted derivative, C_6H_4XY

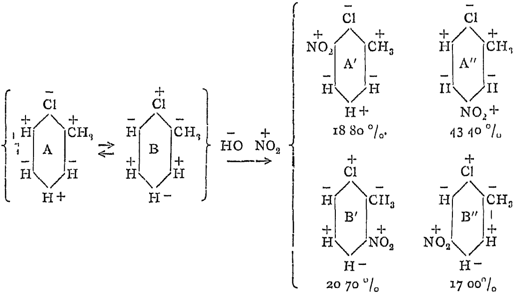
Scheme (1)—*Introduction of a Third Substituent into an Ortho-di-substituted Derivative.*

Here the electronic tautomerism involves two electromers of an ortho-di-derivative These electromers will be designated by the letters A and B while their substitution products will be indicated by A′, A″, and B′, B″, respectively The general scheme (1) for the introduction of the third substituent Z is as follows:—



Theoretically and electronically four tri-substituted isomers are obtainable, namely, A′ and A″ from electromer A; and B′ and B″ from electromer B A remarkable experimental confirmation of this scheme is found in the work of Wibaut[78] who showed that the nitration at 0° of *o*-chlorotoluene yielded all four possible mono-nitro-compounds in considerable quantity.

The electronic interpretation is embodied in the following equations, which are perfectly comparable to the typical equations of scheme (1) above The percentage yield of each isomer is indicated beneath its appropriate electronic formula —



It has been shown that $\overset{-}{\mathrm{Cl}} > \overset{+}{\mathrm{Cl}}$, and $\overset{-}{\mathrm{CH_3}} > \overset{+}{\mathrm{CH_3}}$, i e, the chlorine and methyl radicals may tend in general to function negatively rather than positively, but in *o*-chlorotoluene (either electromer A or B) the substituents must be opposite in polarity. This leads to the consideration of a significant question, namely, *will the polarities of the substituents present in the nucleus predetermine in any way the relative quantities of the isomeric derivatives which are formed?* In the simultaneous formation of the isomeric di-substituted derivatives of benzene the polarities of the substituents and the tendencies of certain substituents to function in one way rather than in another way were shown to be related to the relative quantities of the isomers (ortho and para on the one hand, and meta on the other) which were formed. Now in the case of *o*-chlorotoluene the two substituents present naturally tend to function negatively, but, since one must function negatively while the other functions positively, another perplexing question arises, namely, is the tendency for chlorine to function negatively more pronounced than the tendency for methyl to function negatively? An answer to this important question can be approached only in an indirect way by comparing the general stability of methyl alcohol ($\overset{-}{\mathrm{HO}}\ \overset{+}{\mathrm{CH_3}}$) with that of hypochlorous acid ($\overset{-}{HO}\,.\,\overset{+}{Cl}$) The latter is undoubtedly the less stable, since it is readily decomposed by light or heat, whereas methyl alcohol is a comparatively stable compound Now, the instability and decomposition of hypochlorous acid involves the change, as previously shown, from $\overset{+}{Cl}$ to $\overset{-}{Cl}$, and since $\overset{-}{HO}\ \overset{+}{Cl}$ is less stable than $\overset{-}{HO}\ \overset{+}{CH_3}$, naturally it may be assumed that the tendency for chlorine to function negatively is more pronounced than the tendency for methyl to function negatively, i e, $\overset{-}{Cl} > \overset{-}{CH_3}$ Or in equivalent terms, the tendency for methyl to function positively is more pronounced than the tendency for chlorine to function positively, i.e, $\overset{+}{CH_3} > \overset{+}{Cl}$ (The relative tendency for a radical to function in one way rather than in another way may be defined as its *polar stability*)

These relationships lead to the conclusion that of the two electromers (A and B) of *o*-chlorotoluene, the one (A), in which (Cl) is negative and (CH_3) is positive, would predominate, which in turn would indicate that the nitration of *o* chlorotoluene might yield a greater quantity of the nitrochlorotoluenes A′ and A″, than of the nitrochlorotoluenes B′ and B″. *These assumptions are confirmed by the facts,* since Wibaut (loc cit) has determined the yields of the four mono-nitro-*o*-chlorotoluenes to which are assigned, herewith, the abbreviated electronic formulæ in conformity with the preceding scheme of substitution .—

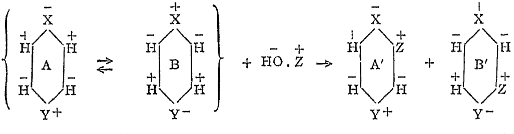
Electromer (A) → (A′), $C_6H_3\ \overset{+}{CH_3}\ \overset{-}{Cl}\ \overset{+}{NO_2}$ (1, 2, 3) .	18·8 per cent
Electromer (A) → (A″), $C_6H_3\ \overset{+}{CH_3}\,.\,\overset{-}{Cl}\,.\,\overset{+}{NO_2}$ (1, 2, 5) .	43·4 " "
	62·2 " "
Electromer (B) → (B′), $C_6H_3\ \overset{-}{CH_3}\,.\,\overset{+}{Cl}\ \overset{+}{NO_2}$ (1, 2, 6) .	20·7 " "
Electromer (B) → (B″), $C_6H_3\ \overset{-}{CH_3}\,.\,\overset{+}{Cl}\,.\,\overset{+}{NO_2}$ (1, 2, 4) .	17·0 " "
	37·7 " "

The combined yields of A′ and A″ total 62·2 per cent. as against 37·7 per cent., the combined yields of B′ and B″

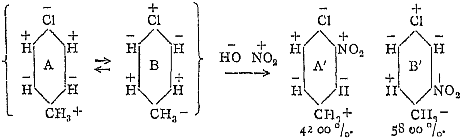
Attention should be called to the fact that the percentage yields of the isomeric products of nitration of ortho-chlorotoluene, in the preceding scheme (1), and also the percentage yields of the isomeric products of nitration of para- and meta-chlorotoluene in the following schemes (2) and (3) respectively, were determined by physical methods—processes of fractional crystallization and comparison of curves of fusion of mixtures of unknown composition with those of known composition

Scheme (2)—Introduction of a Third Substituent into a Para-di-substituted Derivative

Consider now the introduction of a third substituent into a para-di-substituted derivative of benzene according to the following scheme (2) —



Theoretically and electronically, two and only two tri-substituted derivatives are possible, namely, A′ and B′ from electromers A and B respectively One of several series of experiments which confirm the above scheme is the nitration at 0° of *p*-chlorotoluene by Holleman,[79] who demonstrated that only two mono-nitro-*p*-chlorotoluenes were produced. The correlation of these facts with the electronic formulæ is embodied in the following scheme —

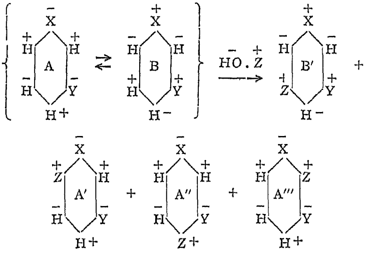


Since $\overset{-}{Cl} > \overset{-}{CH_3}$, or $\overset{+}{CH_3} > \overset{+}{Cl}$, one would be disposed to assume that electromer A would predominate and, accordingly, the nitration of para-chlorotoluene would be expected to yield a greater quantity of A′, $C_6H_3\ \overset{+}{CH_3}.\overset{-}{Cl}\ \overset{+}{NO_2}$ (1, 4, 3), than of B′, $C_6H_3.\overset{-}{CH_3}\ \overset{+}{Cl}\ \overset{+}{NO_2}$ (1, 4, 2) This assumption is not realized since the yields are 42·00 per cent of A′ and 58·00 per cent of

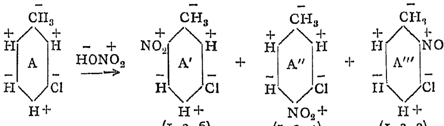
B′ This leads to the assumption that the relative polar stabilities of substituents in para position to each other may differ from the relative polar stabilities of the same substituents when in the ortho position to each other. For example, in the preceding scheme (1) for the nitration of ortho-chlorotoluene, electromer A predominates, but in scheme (2) for the nitration of para-chlorotoluene, electromer B predominates Hence, in scheme (2) the speed of interaction of electromer B with nitric acid is greater than the speed of interaction of electromer A with nitric acid for the yield of B′ is greater than the yield of A′ Thus the speed of interaction of the respective electromers with the substituting reagents determines the yields of the substituted products.

Scheme (3)—*Introduction of a Third Substituent into a Meta-di-substituted Derivative.*

The introduction of a third substituent into a meta-di-substituted derivative of benzene corresponds to the following general scheme —



Since the substituents X and Y occupy positions meta to each other they must be of the same polarity, i e., both are negative in A while both are positive in B. Some interesting theoretical and experimental results present themselves, depending upon the tendencies of X and Y to function positively or negatively. If both X and Y belong to that class of substituents which lead to the formation chiefly of ortho- and para-derivatives (which is the case when $\overset{-}{X} > \overset{+}{X}$ and $\overset{-}{Y} > \overset{+}{Y}$), then electromer A would predominate and the chief substitution products would be A′, A″, and A‴. Furthermore, since X and Y are meta to each other and each is naturally negative, electromer A might predominate to the exclusion of electromer B, and the introduction of a third substituent $\overset{+}{Z}$ would lead to the formation of only three isomeric tri-substitution products, namely, A′, A″, and A‴. Just such a case is found in the nitration at 0° of *m*-chloro-toluene by Wibaut (loc. cit.) The percentage yields of the isomers are indicated in the scheme —



(1, 3, 6) 58 00 % (1, 3, 4) 32 30 % (1, 3, 2) 8 80 %

Now it has been shown in some instances that the tendency for chlorine to function negatively is more pronounced than the tendency for methyl to function negatively, i e , $\overset{-}{Cl} > \overset{-}{CH_3}$. This leads to the assumption that the entering positive nitro radical would be more subject to the directing influence of $\overset{-}{Cl}$ than of $\overset{-}{CH_3}$ Now $\overset{-}{Cl}$ directs $\overset{+}{NO_2}$ to the para position rather than to the ortho position, since chlorobenzene on nitration yields 69·90 per cent of *p*-nitrochlorobenzene, and 30·10 per cent of *o*-nitro-chlorobenzene On the other hand, $\overset{-}{CH_3}$ directs $\overset{+}{NO_2}$ to the ortho position rather than to the para positions since toluene on nitration yields 56 00 per cent. of the *o*- and 40 90 per cent. of the *p*-nitrotoluene. Accordingly, when *o*-chlorotoluene is nitrated, one should expect the greatest yield to be that of isomer (A′) in which $\overset{+}{NO_2}$ occupies a position para to $\overset{-}{Cl}$ and ortho to $\overset{-}{CH_3}$ A smaller yield would be predicted for that isomer (A″) in which $\overset{+}{NO_2}$ is ortho to $\overset{-}{Cl}$ and para to $\overset{-}{CH_3}$. The smallest yield would be predicted for the isomer (A‴) in which $\overset{+}{NO_2}$ is ortho to $\overset{-}{Cl}$ and ortho to $\overset{-}{CH_3}$ These assumptions are fully confirmed by the facts since the respective yields of the three isomers, A', A'', and A''', are, respectively, 58·00 per cent, 32 00 per cent, and 8 80 per cent This constitutes a further proof that the polarities of the substituents in the nucleus and their tendencies to function in one way rather than in another way predetermine not only the type of substitution but also the relative quantities of the isomers produced.

Returning again to the general scheme (3) above, it should be noted that if X and Y belong to that class of substituents which lead to the formation chiefly of meta derivatives, which is the case when $\overset{+}{X} > \overset{-}{X}$ and $\overset{+}{Y} > \overset{-}{Y}$, then electromer B would predominate Accordingly, the introduction of a third substituent Z would lead to the formation chiefly of the tri-substitution product in which all three substituents (X, Y, and Z) are positive Many examples are found in the literature which show that when the substituents in the nucleus are positive, the entering substituent assumes a position meta to those present, and the predominating isomer corresponds to B′, the derivative of electromer B Exact quantitative data upon the amounts of the other possible isomers have not been found in the literature

Having considered all of the possibilities which might be encountered in the introduction of a third substituent Z into an ortho-, a para-, and a meta-di-substituted derivative, C_6H_4XY, of benzene, and having shown that experimental facts and data are in agreement with the theoretical deductions, with the electronic formulæ, and the principle of electronic tautomerism, and with the general electronic rule for substitution, it should be added that the formation of other poly-substituted derivatives of benzene will conform in general to the principles and rule previously developed and illustrated This claim is warranted by a careful study of the numerous tables of the variously substituted derivatives of benzene which have been compiled with great care and presented by Holleman (loc. cit) in his extended work on the influence of the substituents in the benzene nucleus, and the principles of substitution

CHAPTER XII.

THE ACTION OF SODIUM METHYLATE ON THE PRODUCTS OF NITRATION OF THE ORTHO-, PARA-, AND META-CHLOROTOLUENES

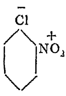
IN the preceding chapter it was shown that unless ortho-, para-, and meta-chlorotoluene manifest the phenomenon of electronic tautomerism it would be impossible to explain the simultaneous formation of the variously substituted isomeric nitro-derivatives when the chlorotoluenes are nitrated The principle of electronic tautomerism involved in the explanation of these substitution reactions will receive further experimental confirmation if it is possible to show by hydrolytic reactions that some of the nitro-derivatives are the products of the interaction of one of the electromers of a chlorotoluene while the other isomeric nitro-derivatives simultaneously formed are the products of nitration of the other electromer of the chlorotoluene.

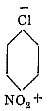
To this end, attention must be directed throughout this chapter to schemes (1), (2), and (3) of the preceding chapter for the nitrations respectively of (1) ortho-, (2) para-, and (3) meta-chloronitrobenzene These schemes constituted the electronic explanation of the nitration reactions conducted by Wibaut, Holleman and Wibaut, respectively, who determined the percentage yields of the several isomers of each nitration by physical methods—processes of fractional crystallization and comparisons of curves of fusion of mixtures of unknown composition with those of known composition.

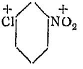
In each of these schemes it will be observed that the electronic formulæ of the isomeric nitration products (A′, A″, etc) of the electromer A embody negative chlorine while those (B′, B″, etc.) of electromer B embody positive chlorine. Now, if it be possible to show by quantitative chemical methods that the yields of the isomers (chloronitrotoluenes) which contain negative chlorine are commensurate with the yields of the same isomers ascertained by Holleman and Wibaut by physical methods, then the conception of the electronic tautomerism of the chlorotoluenes as indicated in schemes 1, 2, and 3 is, to this extent, further substantiated.

The chemical method for the determination of the yields of the isomers containing negative chlorine depends, first, upon the completeness of their interaction with sodium methylate and, second, the non-interaction of the isomers containing positive chlorine. In order to test the applicability of these two points, the action of sodium methylate in methyl alcohol solution upon *o*-, *p*-, and *m*-chloronitrobenzenes was investigated These isomers were chosen because it is commonly recorded that the *o*- and *p*-isomers exchange their halogen atom for OH, $O(CH_3)$, or NH_2, while the *m*-isomer is non-reactive.

An interpretation of these reactions has been given in Chapter VIII, Section A, from the standpoint of the electronic formula of benzene and the substitution rule The abbreviated electronic formulæ of the chloronitrobenzenes are as follows·—







Only those isomers containing negative halogen (*o*- and *p*-) should interact with sodium methylate, thus

$$\overset{+}{NO_2}\ C_6H_4\ \overset{-}{Cl} + \overset{+}{Na}.\overset{-}{OCH_3} \rightarrow \overset{+}{NO_2}\ C_6H_4\ \overset{-}{OCH_3} + \overset{+}{Na}\ \overset{-}{Cl},$$

and the *m*-isomer, containing positive chlorine, should be non-reactive under the same conditions

The extent of the replacement of negative chlorine can be found by determining the quantity of sodium chloride liberated. After repeated experiments, designed to secure the conditions noted, the following method was found to yield theoretical results About 0.2 gram of the chloronitrobenzene was dissolved in 15 c.c of a normal solution of sodium methylate in absolute methyl alcohol The solution was heated at 100° in a sealed glass tube for 5 hours The contents of the tubes were then diluted to a volume of 200 c.c., acidified with nitric acid, boiled to expel the methyl alcohol, cooled, and filtered. The quantity of sodium chloride in the respective filtrates was determined by titration with standard solution of silver nitrate The following results were obtained —

Substance	(Grams)	No. c.c. 0·0957N $AgNO_3$ Solution	Per Cent Negative Cl Found	Per Cent Negative Cl Theoretical
o-$\overset{-}{\text{Cl}}$ C_6H_4 $\overset{+}{\text{NO}_2}$	0·2005	12·81	22·56	22·51
p-$\overset{-}{\text{Cl}}$ C_6H_4 $\overset{+}{\text{NO}_2}$	0·2007	12·78	22·48	22·51
m-$\overset{+}{\text{Cl}}$ C_6H_4 $\overset{+}{\text{NO}_2}$	0·1992	0·00	0·00	0·00

These results show conclusively that isomers containing negative chlorine may be estimated quantitatively, provided conditions are secured for their complete interaction with sodium methylate, while under the same conditions the isomer containing positive chlorine is non-reactive

The chief problem of this investigation was to secure conditions under which the negative halogen atoms of the nitration products of *o*-, *p*-, and *m*-chlorotoluenes would completely interact with sodium methylate and thus afford a chemical method for determining the percentage yields of the isomers of chloronitrotoluene which contain negative chlorine. A comparison of the chemically determined and the physically determined yields could then be made With this end in view, *o*-, *p*-, and *m*-chlorotoluenes were each separately nitrated (at 0°) according to the specific directions given by Wibaut, Holleman and Wibaut, respectively The methods were originally designed to yield only mono-nitro substitution products. The respective products of nitration of each of the chlorotoluenes, which consisted of mixtures of the different isomers (nitrochlorotoluenes), as indicated in the preceding schemes 1, 2, and 3, were treated with sodium methylate solutions of varying concentrations—0·5 *N*, *N*, 2 *N*, and 3 *N* Samples, 0·2 to 0·4 gram, of the nitration products were heated, each with 15 c.c. of the sodium methylate solution in sealed tubes, for 10 hours at 100° The contents of the tubes were then analysed, as previously described, for the negative chlorine, liberated as $\overset{+}{\text{Na}} . \overset{-}{\text{Cl}}$, precipitated and weighed as silver chloride The percentage yield of the combined isomers containing negative chlorine was calculated from the ratio

$\overset{+}{\text{Ag}}\ \overset{-}{\text{Cl}} \cdot \overset{-}{\text{Cl}}, \overset{+}{\text{NO}_2}\ \overset{+}{\text{CH}_3} . \text{C}_6\text{H}_3$. The results of these experiments are recorded in three sections (I., II., and III.) to correspond with schemes 1, 2, and 3 for the nitration of *o*-, *p*-, and *m*-chlorotoluenes, respectively. All reactions were conducted in duplicate.

TABLE I

I. Action of Sodium Methylate on the Isomers Derived from *o*-Chlorotoluene

(See Scheme 1.)

Mixture of Isomers (gram)	Normality NaOCH$_3$	AgCl (gram)	Per Cent yield of Isomers A′ + A″ (1, 2, 6 and 1, 2, 4- $\overset{-}{\text{Cl}}$, $\overset{+}{\text{CH}_3}$, $\overset{+}{\text{NO}_2}$, C$_6$H$_3$)	Average
0·2625	0·5 *N*	0·1163	53·01	53·15
0·2434	0·5 *N*	0·1084	53·29	
0·2835	*N*	0·1388	58·58	58·73
0·2938	*N*	0·1446	58·89	
0·3283	2 *N*	0·1362	49·64	49·88
0·2994	2 *N*	0·1254	50·12	
0·2772	3 *N*	0·0884	38·16	38·23
0·2940	3 *N*	0·0941	38·30	

These results indicate that the extent of the reaction with sodium methylate is greatest in the normal solution. A 58·73 per cent. yield of the combined isomers containing negative chlorine was obtained. The yields of these isomers determined by the physical methods of Wibaut total 62·20 per cent. The yields obtained by the two methods, while not identical, approximate closely. Variations will be considered later.

TABLE II

II. Action of Sodium Methylate on the Isomers Derived from *p*-Chlorotoluene

(See Scheme 2.)

Mixture of Isomers (gram)	Normality NaOCH$_3$	AgCl (gram)	Per Cent. Yield of Isomer A′ (1, 2, 4 $\overset{-}{\text{Cl}}$, $\overset{+}{\text{NO}_2}$, $\overset{+}{\text{CH}_3}$, C$_6$H$_3$)	Average
0·2707	0·5 *N*	0·0799	35·33	35·23
0·2868	0·5 *N*	0·0842	35·13	
0·3068	*N*	0·0946	36·89	36·18
0·2608	*N*	0·0773	35·47	
0·2854	2 *N*	0·0750	31·44	30·93
0·3068	2 *N*	0·0780	30·42	
0·3297	3 *N*	0·0814	29·54	29·92
0·3037	3 *N*	0·0769	30·30	

Here also the extent of the reaction with sodium methylate was greatest in the normal solution, which indicated a yield of 36·18 per cent of the isomer containing negative chlorine The yield of the same isomer determined by Holleman (fusion curve method) was 42·00 per cent.

TABLE III

III. Action of Sodium Methylate on the Isomers Derived from *m*-Chlorotoluene.

(See Scheme 3)

Mixture of Isomers (gram)	Normality $NaOCH_3$	AgCl (gram)	Per Cent Yield of Isomers $A' + A'' + A'''$, 1, 3, 6 + 1, 3, 4 + 1, 3, 2-$\overset{-}{CH_3}$, $\overset{-}{Cl}$, $\overset{+}{NO_2}$, C_6H_3	Average
0·2257	0·5 *N*	0·1652	87·59	87·77
0·2510	0·5 *N*	0·1843	87·86	
0·2672	*N*	0·1987	88·99	88·49
0·2520	*N*	0·1853	87·99	
0·2670	2 *N*	0·1898	85·06	85·52
0·3212	2 *N*	0·2308	85·98	
0·2809	3 *N*	0·1923	81·92	81·19
0·2808	3 *N*	0·1888	80·46	

Again the extent of the reaction was greatest in the normal solution indicating a yield of 88·49 per cent. of the three isomers containing negative chlorine. Wibaut (fractional crystallization and fusion curve methods) obtained a 100 per cent. yield of these isomers

The yields of the isomers containing negative chlorine determined by physical methods and the maximum yields of the same isomers determined by the chemical methods just described are summarized in the following table :—

TABLE IV

Scheme	Isomers	Physical.	Chemical.	Percentage Ratio
1	(A′ + A″)	62·20 (Wibaut)	58·73 (Fry)	94·42
2	(A′)	42·00 (Holleman)	36·18 „	86·14
3	(A′ + A″ + A‴)	100·00 (Wibaut)	88·49 „	88·49

The extreme care with which Holleman and Wibaut conducted their physical determinations leads one to accept their results as practically final. Accordingly, in the last column above, the chemically determined yields are recorded as percentages of the physically determined yields. If each of the values in the last column was 100 per cent then it might be asserted without question that the conception of the electronic tautomerism of the *o*-, *p*-, and *m*-chlorotoluenes given in schemes 1, 2, and 3, respectively, is completely substantiated by chemical methods It may, nevertheless, be maintained that in so far as the values in the last column do approach the theoretical, so far, at least, do they substantiate both by physical and by chemical methods the electronic tautomerism of the chlorotoluenes. Moreover, it may be said that the electronic tautomerism of *o*-, *p*-, and *m*-chlorotoluenes is the only hypothesis that has accounted for the replaceability of certain halogen atoms in some of the isomeric nitrochlorotoluenes and the non-replaceability of certain halogen atoms in others The data presented in this chapter substantiate the hypothesis.

The fact that the chemically determined quantities of the isomers containing negative chlorine were less than the quantities determined by physical methods may have been due to two causes First, the interaction with sodium methylate of one or more of these isomers in the mixtures may have been incomplete This is not likely, since the results of the experiments with the analogous chloronitrobenzene gave results in perfect agreement with the theory Furthermore, a survey of the quantitative data given in connection with schemes 1, 2, and 3 shows a maximum replacement in every reaction in which the uninormal solutions of sodium methylate were used Concentrations below or above normal gave lower yields

In the second place, the low yields of the isomers containing negative chlorine may be due to the fact that the relative quantities of the isomers obtained on nitration of the chlorotoluenes in Holleman's laboratories may not have been identical with the relative quantities of the same isomers obtained in this laboratory, even though the original directions given by Holleman and Wibaut were carried out precisely. The variations are most likely due to lack of standardization in certain details of manipulation, such as the rate of the addition of the nitric acid, methods of stirring, cooling, etc. While the temperature variations were kept within the prescribed limits, primarily to avoid the formation of poly-nitro-derivatives, it is quite likely that the local temperature effects in the reaction mixture may have altered the relative quantities of the isomers formed. In fact, I have found that when nitrations were conducted separately, but under identical conditions, variations in the fusion points of the resulting mixtures were noted This signifies corresponding variations in the relative quantities of the isomers in these mixtures

In conclusion, the variations between the chemically and the physically determined yields are not sufficient to invalidate the principle of the electronic tautomerism of the chlorotoluenes The conception affords a consistent interpretation of the observed facts, and is substantiated in a great measure by the quantitative data offered in this chapter A one hundred per cent quantitative confirmation of the electronic tautomerism of the mixed dihalogen benzenes (notably para-chlorobromobenzene) is found in the experimental data presented in Chapter X Indeed, the agreement between experiment and hypothesis, definitely indicated in Chapters X, XI and XII, establishes the principle of the electronic tautomerism of benzene derivatives This principle makes it possible to interpret the simultaneous formation of ortho-, para-, and meta- di-substituted, and poly-substituted derivatives of benzene

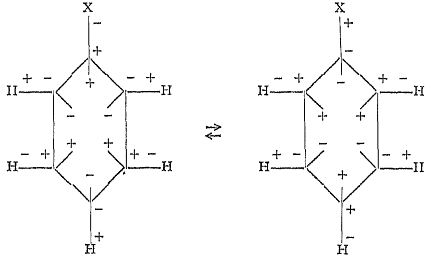
CHAPTER XIII

THE MECHANISM OF SUBSTITUTION IN THE BENZENE NUCLEUS

THE preceding interpretations of substitution reactions dealt with the simplified electronic formula of benzene in which only the polarities of the hydrogen atoms and substituents were indicated. A more comprehensive description of the mechanism of substitution reactions requires that some account be taken of the part played by the centric valences or double bonds of the benzene nucleus. The first part of this discussion relates to the mechanism of the electronic tautomerism of benzene derivatives.

A. The Mechanism of Electronic Tautomerism of Benzene Derivatives.

The important part played by the principle of electronic tautomerism in the explanation of substitution in the benzene nucleus leads to the consideration of a mechanism which involves the centric valences of the carbon atoms of the nucleus. The key to this mechanism is embodied in the assumption (to be substantiated by experimental facts) that when a given hydrogen atom or substituent is negative it is united to a carbon atom which possesses a positive centric valence. On the other hand, when a hydrogen atom or substituent is positive it is united to a carbon atom which possesses a negative centric valence. These assumptions are embodied in the following formulæ illustrating more completely the electronic tautomerism of a mono-substituted derivative



The electronic tautomerism of a poly-substituted derivative would conform to the same principles and like scheme

When $\overset{-}{X}$ becomes $\overset{+}{X}$ ($\overset{-}{X} \rightarrow \overset{+}{X} + 2\ominus$) the polarity of the carbon valence binding X is changed from positive to negative, i e, in terms of the electronic conception of oxidation and reduction, the positive valence has been reduced to a negative valence On the other hand, when $\overset{+}{X}$ becomes $\overset{-}{X}$, the valence binding X is changed from negative to positive, i e, it is oxidized Simultaneously, corresponding changes occur in the polarities of each of the other hydrogen atoms or substituents, and the carbon valences binding same In other words, for each oxidation there is a corresponding reduction, otherwise, the symmetry and, consequently, the stability and composition of the benzene nucleus would be altered

Another important point to be observed in the above scheme is that the transition from the one electromer to the other involves a change in the polarity of each centric valence This type of change is defined as *centric rearrangement.* A complete scheme of the several possible centric formulæ of benzene and their transitions to the Kekulé formulæ will be shown, in a subsequent chapter, to involve changes from double bonds of the type ($\mathrm{C}\overset{+\ -}{\underset{-\ +}{=\!=\!=}}\mathrm{C}$), termed *contraplex*, to double bonds of the type ($\mathrm{C}\overset{+\ -}{\underset{+\ -}{=\!=\!=}}\mathrm{C}$), termed *diplex.* Such changes, *contraplex-diplex transitions*, take place in those compounds which show distinct bands in their absorption spectra[80] Accordingly, they serve as a structural basis for the development of a relationship between chemical constitution and absorption spectra. In other words, the rearrangements of the centric valences and the concomitant contraplex-diplex transitions cause a disturbance in the vibrations of the systems of electrons, whereby light of correlated period is absorbed in accordance with the theory of resonance By means of the various electronic formulæ of benzene and their systems of dynamic equilibria, it will be demonstrated that a definite relationship exists between the oscillation frequencies of the seven bands in the absorption spectrum of benzene and the numbers of contraplex-diplex transitions involved, which function as the origin of the respective absorption bands This relationship is that of a linear function expressed by the equation, $y = 21\ 60628x + 3679{\cdot}509$, in which ($y$) is the oscillation frequency of a given band, and (x) is the number of contraplex-diplex transitions functioning as the origin of the given band The deviations of the calculated frequencies from the observed frequencies are less than the limits of error in experimental observation Other similar and exact relationships are developed and found to hold for the oscillation frequencies of the absorption bands of naphthalene,[81] chlorobenzene and bromobenzene,[82] and for the fluorescence bands of anthracene and phenanthrene [83] This work, which will be fully described later, has been briefly indicated here because through these physical measurements an experimental confirmation is offered for the hypothesis of contraplex-diplex transitions which involve centric rearrangements, i e, changes in the polarities of the centric valences of benzene These centric valences and rearrangements will now be shown to play a very definite part in the further development of the mechanism of substitution in the benzene nucleus

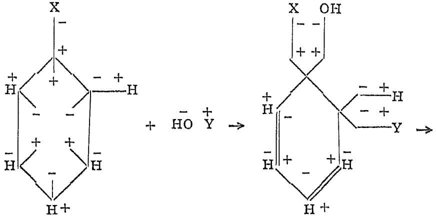
B. The Mechanism of Substitution: an Electronic Interpretation of the Hypothesis of Holleman.

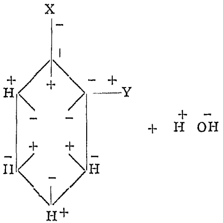
Holleman in his work on *Die direkte Einfuhrung von Substituenten in den Benzolkern*, has described and discussed the various hypotheses which have been advanced at different times to explain the rules of substitution, but he is of the opinion that none of these hypotheses is able to give a satisfactory explanation of the facts. Furthermore, Holleman, in a recent paper,[84] makes this statement —

"Notwithstanding the fact that the problem of substitution in the benzene nucleus has been studied intensively enough of late, there still remains a fundamental question which has not yet been solved, it is the question of knowing the reason why such or such group directs a new substituent chiefly to the para-ortho positions or chiefly to the meta position"

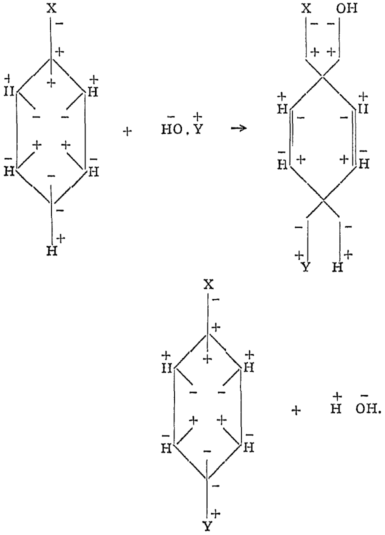
Apropos of this statement, it has been shown that the electronic formula of benzene and the electronic interpretation of the Brown and Gibson rule do afford an explanation, in the sense that if the substituent in the nucleus is negative then the entering positive substituent must assume a position either ortho or para to the substituent already present, and, if the substituent in the nucleus is positive, then the entering positive substituent must assume a position meta to the one already present. This hypothesis has been substantiated by numerous examples of substitution. The mechanism, or schemes, for these reactions as previously presented involved the simplified electronic formulæ for benzene indicating only the polarities of the hydrogen atoms and substituents, and the electronic formulæ of the substituting reagents, but, since it is generally conceded that substitution in the nucleus involves (1) the addition of the substituting reagent (for example, $\overset{-}{HO}\,.\,\overset{+}{Y}$) and (2) the elimination of certain elements (for example, $\overset{+}{H}\ \overset{-}{OH}$), it follows that any mechanism proposed to account for these changes (1 and 2) must consider the part played by the centric valences or the double bonds of the nucleus. For the present, it is simpler to indicate the part played by the free centric valences in effecting the addition of the substituting reagent, rather than to picture the part as played by the "opening up" or "breaking" of the double bonds. In either case, the mechanism of the change involved would amount to one and the same thing, since the centric formula is simply an intermediate phase between the Kekulé formulæ, or phases, which possess double bonds.

From the above points of view a more complete mechanism of substitution will be indicated, first, for the formation of an ortho-di-substituted derivative, in which case the substituent (X) present in the nucleus functions negatively, and the entering substituent (Y) is positive. The formulæ will indicate only the polarities of the bonds or valences which are immediately related to the particular changes.

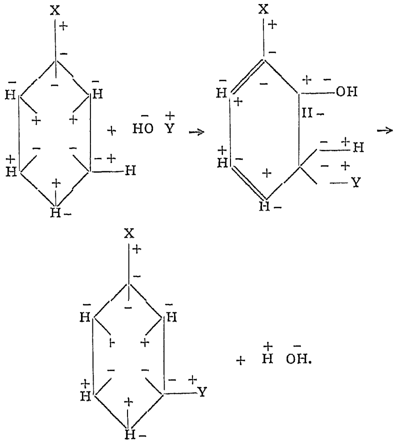




The formation of a para-di-substituted derivative also involves the electromer in which X is negative, and the entering substituent Y, positive



On the other hand, the formation of a meta-di-substituted derivative involves the electromer in which X is positive, and the entering substituent Y is positive.



In each of the above schemes, the addition of the radicals of the substituting reagent ($\overset{-}{\text{HO}}$ and $\overset{+}{\text{Y}}$) engages only two of the six centric valences The remaining centric valences lend themselves to the formation of double bonds in the addition product. This addition reaction is followed by the elimination of $\overset{+}{\text{H}}$ and $\overset{-}{\text{OH}}$ as water and a consequent return to the centric formula of the di-substituted derivative

The substitution of halogen ($Y_2 = \overset{+}{Y} + \overset{-}{Y}$) would correspond to the addition of $\overset{+}{Y}$ and $\overset{-}{Y}$ to the centric valences with the subsequent elimination of $\overset{+}{H} . \overset{-}{Y}$ and the fixing of $\overset{+}{Y}$ in the nucleus, either ortho or para to $\overset{-}{X}$, or meta to $\overset{+}{X}$. In Chapter XV a mechanism is given for the action of halogen carriers in effecting nucleus substitution, which is directly correlated with the above schemes The halogen carrier forms an unstable addition compound with the radicals $\overset{+}{Y}$ and $\overset{-}{Y}$ of the halogen molecule Y_2.

This unstable addition compound either induces the direct combination of $\overset{+}{Y}$ and $\overset{-}{Y}$ with centric valences, or the dissociation products of the addition compound itself combine with the centric valences. In either event, subsequent elimination of $\overset{+}{H} . \overset{-}{Y}$ (and the concomitant regeneration of the carrier) results in the nucleus substitution of $\overset{+}{Y}$.

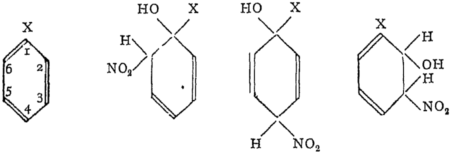
An examination of the preceding mechanisms of substitution shows that the *polarity of the substituent X present in the nucleus and the polarities of the centric valences predetermine the types of substitution which result in the formation either of ortho- and para-derivatives, or of meta-derivatives* If both electromers ($\overset{+}{C_6H_5} . \overset{-}{X}$ and $\overset{-}{C_6H_5}\ \overset{+}{X}$) interact with $\overset{-}{HO}\ \overset{+}{Y}$, simultaneous formation of ortho-, para-, and meta-derivatives follows as previously described and confirmed by extended experimental facts and data.

It may now prove interesting to show that the mechanism for the formation of ortho, para, and meta classes of derivatives as proposed by Holleman may be correlated with the electronic formulæ and substitution schemes just presented.

On the basis of the Kekulé formula (the centric formula applies equally well) Holleman supposes that the substituent X, already present in the nucleus, may either promote or retard the addition of the radicals of the substituting reagent to the double bonds (or to the centric valences). If X promotes addition, the ortho and para compounds are formed, addition having taken place in position 1, 2 (or 1, 6) and 1, 4 respectively "Conjugation" is assumed to cause the addition in the para (1, 4) position according to Thiele's hypothesis On the other hand, the addition of the substituting reagent to the double bond (or to the centric valences) of carbon atoms 2 and 3 cannot be greatly influenced by X, because X is not in direct relation with either of these atoms In other words, under the influence of X, the speed of addition to position 1, 2 (or 1, 6) and 1, 4 is either accelerated or retarded, while the speed of addition to position 2, 3 (or 5, 6) is about the same as in the non-substituted benzene itself Accordingly, when X accelerates the reaction, substitution takes place in positions ortho and para; when the acceleration is great, the ortho and para products will be formed exclusively, for the quantity of the meta product which could be formed simultaneously through addition to position 2, 3 is then so small that it is not perceptible. When, on the other hand, the acceleration is not so great, the meta isomer may also be formed.

In the case where X retards the reaction, the addition to position 2, 3 predominates and proceeds more rapidly than the addition to position 1, 2 (or 1, 6) and 1, 4. The meta isomer then becomes the principal product.

Holleman illustrates the mechanism of these types of addition by supposing C_6H_5X to undergo nitration, in which case nitric acid adds as HO and NO_2. The addition compounds are as follows:—



Ortho Para Meta

By the subsequent removal of H and OH as water, an ortho, a para, or a meta compound is formed.

Now it should be noted that the above addition compounds as formulated by Holleman are identical with the electronic formulæ for the addition compounds previously indicated, but with this important exception: the electronic formulæ, by indicating the polarities of the hydrogen atoms, the substituents, the centric valences, and the radicals of the substituting reagent, make possible *a formula-mechanism by which addition must take place in one way rather than in some other way*. On the other hand, the ordinary Kekulé and centric formulæ cannot, *per se*, indicate why addition should proceed in one way rather than in another. For instance, the addition of HO . NO_2 in Holleman's scheme unites OH to carbon atom 1, and NO_2 to carbon atom 6. Now as far as the regular Kekulé or centric formula is concerned OH might just as well unite to atom 6 while NO_2 unites to atom 1. Other additions are structurally possible in positions 1, 4 and 2, 3. In other words, six types of addition instead of the three as indicated by Holleman are possible from the standpoint of the ordinary structural formulæ Hence, *it is evident that some qualification or limitation of the types of addition must be made* This, of course, is true of any hypothesis which deals with structural formulæ and proposed mechanisms of reaction, but the marked superiority of electronic formulæ over ordinary structural formulæ lies in the fact that the valences of the atoms and radicals may be qualified, in conformity with facts of experiments, as positive or negative, a distinction which cannot be embodied in the ordinary formulæ. Therefore, the electronic valence hypothesis which permits of such qualifications possesses greater significance in the interpretation of chemical phenomena than the ordinary valence hypothesis.

It may now be demonstrated that Holleman's formulæ for the ortho, para, and meta addition compounds may be interpreted in terms of positive and negative valences Furthermore, this interpretation logically leads to the same electronic formulæ that were proposed for these addition compounds in the first part of this section (B) This necessarily follows if we admit that the electronic formulæ of water and nitric acid are $\overset{+}{H}\ \overset{-}{OH}$ and $\overset{-}{HO}.\overset{+}{NO_2}$, respectively, and, that the benzene molecule is symmetrically constituted, i e., from the electronic point of view that for every positive charge or valence there is a corresponding negative charge or valence. The correlation of Holleman's formulæ with the electronic formulæ is as follows:—

In Holleman's ortho addition compound, the union of $\overset{-}{OH}$ with carbon atom 1, and $\overset{+}{NO_2}$ with carbon atom 2 or 6, means that the free valence of atom 1 is positive while that of atom 2 or 6 is negative In the para addition compound, $\overset{+}{NO_2}$ unites to carbon atom 4 which, accordingly, possesses a free negative valence In other words, the ortho and para addition compounds show that the centric valences of positions 2, 4, and 6 are negative while 1 is positive. Consequently, from the symmetry standpoint, the centric valences of positions 3 and 5 are positive just as 1 is positive

The polarities of the hydrogen atoms and substituents of the nucleus are indicated by Holleman's assumption that the disubstituted derivative is formed through the elimination of water

$\overset{+}{H}\,.\,\overset{-}{OH}$. In Holleman's formula for the ortho addition compound, the hydrogen atom of position 2 or 6 is eliminated with the hydroxyl radical of position 1, and in the para addition compound the hydrogen atom of position 4 is likewise eliminated with hydroxyl of position 1 Since the elimination of water is the union of $\overset{+}{H}$ and $\overset{-}{OH}$, it follows that the hydrogen atoms of positions 2, 4, and 6 of the ortho and para nitro-compounds of Holleman are positive. Consequently, from the symmetry standpoint, the hydrogen atoms or substituents of position 1, 3, and 5 are negative As a matter of fact, the ortho and para nitro-compounds, in which X = Cl or Br, readily exchange X for hydroxyl on treatment with aqueous potassium hydroxide, since OH is negative, X is accordingly negative

Having correlated Holleman's ortho and para compounds with the electronic formulæ, consider, on the other hand, his formula for the meta addition compound Here, $\overset{-}{HO}$ unites with the free valences of carbon atoms 2 or 6, while $\overset{+}{NO_2}$ combines with those of atoms 3 or 5 Hence, the free or centric valences of positions 2 and 6 are positive while those of positions 3 and 5 are negative, and from the electronic symmetry standpoint, the remaining centric valences of positions 1 and 4 must be negative and positive, respectively Thus in the meta nitro-compound the centric valences of carbon atoms 1, 3, and 5 are negative while those of atoms 2, 4, and 6 are positive Considering the polarities of the hydrogen atoms and substituents, $\overset{+}{NO_2}$ replaces the hydrogen atom of position 3 or 5, which is accordingly positive From the symmetry standpoint X of position 1 should also be positive As a matter of fact, when X = NO_2, as in nitrobenzene ($\overset{-}{C_6H_5}\,.\,\overset{+}{NO_2}$), the entrance of a second $\overset{+}{NO_2}$ is in position 3 or 5, meta to position 1 Furthermore, when X = Cl or Br in the meta nitro-compounds, X is not directly replaceable by negative hydroxyl and is therefore positive The atoms of positions 1, 3, and 5 being positive, those of positions 2, 4, and 6 are negative

From the above it is evident that Holleman's formulæ and mechanism of substitution may be interpreted in terms of positive and negative valences, and the electronic formulæ thereby developed are correlated perfectly with the electronic formulæ and principles previously presented Therefore, the numerous cases of substitution which have been interpreted by Holleman's hypothesis are also interpreted by the electronic formulæ and principles which possess the added significance of showing why certain substituents (which are negative) lead to the formation of ortho- and para-derivatives, while others (which are positive substituents) lead to the formation of meta-derivatives

The remaining features of Holleman's substitution hypothesis to be considered from the point of view of positive and negative valence relate to the velocities of the substitution reactions and their dependence upon the nature of the substituents which are present in the nucleus Thus, when a substituent, X, accelerates the substitution reaction, substitution follows the ortho-para rule which may lead to the exclusion of any meta compound If X has no such accelerating effect, smaller or larger quantities of the meta compound will be formed. These facts make it possible to predict the place that a third substituent C will occupy in the nucleus of a di-substituted derivative, C_6H_4AB This place is determined by Holleman by measuring the speeds of substitution of C in C_6H_5A and in C_6H_5B, and by ascertaining the proportions in which the isomers of C_6H_4AC and C_6H_4BC are formed in each case A comparative study from these points of view enables Holleman to determine the relative effects of different substituents upon the speeds of substitution reactions. Thus, one substituent, HO, is found to have a greater accelerating effect than another, NH_2 (represented thus $OH > NH_2$), and a comparison of these relative effects leads to a series For instance, the substituents which lead to the formation of ortho- and para-derivatives are arranged thus $OH > NH_2 > \text{halogens} > CH_3$ The substituents which lead to the formation of meta-derivatives present the series $CO_2H > CHO > SO_3H > NO_2$.

Apropos of his hypothesis, Holleman has just recently stated that the cause for the different accelerating effects of the different substituents has not yet been explained. This "cause" may be interpreted in terms of the electronic conception of positive and negative valences, because the types of substitution are directly related to the polarities of the substituents present in the nucleus and the tendencies of these to function in one way rather than in another way For instance, as shown in Section B of Chapter IX, those substituents which lead chiefly to the formation of ortho- and para-derivatives are the substituents which tend to function negatively rather than positively ($\overset{-}{X} > \overset{+}{X}$), while those substituents which lead chiefly to the formation of the meta compound are the very substituents which tend to function positively rather than negatively ($\overset{+}{X} > \overset{-}{X}$) Moreover, a substituent which is naturally negative may manifest a greater tendency to function negatively than another negative substituent, thus $\overset{-}{X} > \overset{-}{Y}$, and analogously for positive substituents there exists the relation ($\overset{+}{X} > \overset{+}{Y}$) These respective tendencies were shown in Chapter XI to be a possible cause for the preponderance of one electromer over another in the electronic tautomerism of benzene derivatives This preponderance or increased concentration, in turn, accounted for the relative yields of the several possible isomers Therefore, if the greater concentration of one electromer in the equilibrium system is determined by the tendencies of its substituents to function in one way rather than in another way, and if the speed of a reaction is a factor of the concentrations of the interacting substances, it follows that the speed of a substitution reaction is dependent upon the polarities of the substituents present in the nucleus and their respective tendencies to function in certain ways From this point of view it follows that Holleman's series

$$(OH > NH_2 > \text{halogens} > CH_3)$$

may be represented thus $\overset{-}{OH} > \overset{-}{NH_2} > \overset{-}{\text{halogens}} > \overset{-}{C}H_3$ The other series is as follows. $\overset{+}{C}O_2H > \overset{+}{C}HO > \overset{+}{S}O_3H > \overset{+}{N}O_2$

If the tendency for a substituent to function in one way rather than in another way be defined as the "polar stability of the substituent," it follows that *the velocities of substitution re-* † *actions in the benzene nucleus are functions of the polar stabilities of the substituents in the nucleus.* In other words, the polar stabilities of the substituents determine the concentrations of the electromers, which concentrations are the principal factors in determining the velocities of the substitution reactions.

This chapter should be concluded with the following summary

The conception of the electronic tautomerism of the derivatives of benzene furnishes an explanation of (1) the types of substitution and the simultaneous formation of ortho-, para-, and meta-substituted derivatives, (2) it renders possible the prediction of the relative yields of the isomers which are dependent upon the preponderance or increased concentration of one electromer over the other, (3) the concentrations of the electromers are predetermined by the *polar stabilities* of the substituents in the nucleus, (4) the velocities of substitution reactions are functions of the polar stabilities of the substituents. Accordingly all facts that are explained in terms of the velocities of reactions may be interpreted in terms of the polar stabilities of the substituents. This phase of substitution in the benzene nucleus will be developed further in the following chapter.

CHAPTER XIV.

THE QUANTITIES OF THE PRODUCTS OF NITRATION OF VARIOUS DERIVATIVES OF BENZENE IN RELATION TO THEIR ELECTRONIC FORMULÆ.

THE two most important phases of the problem of substitution in the benzene nucleus are (1) the explanation of the *types* of substitution, that is, the conditions which predetermine the formation of ortho-, para-, and meta-substituted derivatives, and (2) the possibility of predicting within certain limits the relative *quantities* of the resulting substitution products The first phase of this problem has been explained by the electronic formula of benzene, and the principle that the polarity of the substituent X present in the nucleus, and the polarities of the centric valences predetermine the types of substitution, namely, the formation of ortho- and para-derivatives, or of meta-derivatives. Electronic tautomerism of benzene derivatives accounts for the simultaneous formation of ortho-, para- and meta-derivatives.

It is the purpose of the present chapter to suggest a method of attacking the second phase of the benzene substitution problem relating to the quantities of the substitution products obtained. A possible solution will be indicated in a study of the quantitative yields of the products of nitration of various derivatives of benzene in conjunction with the electronic formulæ of these derivatives

In the preceding chapter it was shown that a relationship must exist between the concentrations or reactivities, of the electromers of a given benzene derivative in tautomeric equilibrium ($\overset{+}{C_6H_5} . \overset{-}{X} \rightleftharpoons \overset{-}{C_6H_5} . \overset{+}{X}$), and the yields of the respective products of nitration of each electromer This follows from the fact that there is a relationship between the concentration of a given electromer and its speed of interaction with nitric acid, for if electromer $\overset{+}{C_6H_5}\ \overset{-}{X}$ preponderates, then the combined yields of the ortho- and para-derivatives of $\overset{+}{C_6H_5} . \overset{-}{X}$ will exceed the yield of the meta-derivative of $\overset{-}{C_6H_5} . \overset{+}{X}$ On the other hand, if electromer $\overset{-}{C_6H_5} . \overset{+}{X}$ preponderates, then the yield of the meta-derivative will be greater than the combined yields of the ortho- and para-derivatives

It has been assumed that the preponderance or increased concentration of one electromer over the other depends upon, or is a function of, the tendency of the given substituent to function in one way rather than in another, thus, either $\overset{-}{X} > \overset{+}{X}$ or $\overset{+}{X} > \overset{-}{X}$ This tendency has been referred to, in the preceding chapter, as the *polar stability* of the substituent Accordingly, the concentrations of the electromers are predetermined by the polar stabilities of the substituents present in the benzene nucleus

It now becomes necessary to develop further this conception of polar stability and to inquire how and to what extent it predetermines the types of substitution, and, concomitantly, the quantitative yields of the substitution products To this end, the nitration of toluene, benzyl chloride, benzal chloride, and benzotrichloride, quantitatively investigated by Holleman,[85] affords significant data which are given in the following table —

	C_6H_5 X	Y	Ortho	Para.	(*o* + *p*)	Meta
1	C_6H_5 CH_3	NO_2	58·8	36·8	95·6	4·4
2	$C_6H_5 . CH_2Cl$	NO_2	40·9	54·9	95·8	4·2
3	C_6H_5 $CHCl_2$	NO_2	23·3	42·9	66·2	33·8
4	C_6H_5 CCl_3	NO_2	6·8	28·7	35·5	64·5

The first column embodies the formulæ of the mono-substituted derivatives, C_6H_5 X, which are nitrated at or near 0° Centigrade, under conditions that lead to the substitution of only one nitro group, Y, yielding in each of the nitration reactions (Nos 1, 2, 3, and 4) varying quantities of ortho-, para- and meta-nitrotoluenes, C_6H_4XY. The fifth column gives the combined yields of ortho- and para-derivatives, while the sixth column shows the corresponding yields of meta-nitrotoluene.

From the standpoint of the scheme for the nitration of a mono-substituted derivative, C_6H_5X, yielding simultaneously ortho-, para-, and meta-di-substituted derivatives, C_6H_4XY

(see p. 78), the above data show that the tendency for the substituent X to function negatively is greater in $C_6H_5 \cdot CH_3$, and in $C_6H_5 \cdot CH_2Cl$, than it is in either $C_6H_5 . CHCl_2$ or $C_6H_5 \cdot CCl_3$. This tendency, or relative polar stability, is represented thus: $\overset{-}{C}H_3$ or $\overset{-}{C}H_2Cl > \overset{-}{C}HCl_2 > \overset{-}{C}Cl_3$. Consequently, the combined yields of the ortho- and para-nitrotoluenes, while practically the same in the nitration of $C_6H_5 \cdot CH_3$ and $C_6H_5 . CH_2Cl$, are found to decrease when $C_6H_5 \cdot CHCl_2$ and $C_6H_5 \cdot CCl_3$ are nitrated. In other words, the concentrations of the electromers of the type $\overset{+}{C_6H_5}\ \overset{-}{X}$ in the successive nitrations 1, 2, 3, and 4 (preceding table) are relatively as follows:—

$$\overset{+}{C_6H_5}\ \overset{-}{CH_3}, \text{ or } \overset{+}{C_6H_5}\ \overset{-}{CH_2Cl} > \overset{+}{C_6H_5} . \overset{-}{CHCl_2} > \overset{+}{C_6H_5}\ \overset{-}{CCl_3}$$

On the other hand, it may be noted that the tendency for the substituent CCl_3 to function positively is greater than that of either $CHCl_2$ or CH_2Cl and CH_3. These relative polar stabilities are indicated thus: $\overset{+}{C}Cl_3 > \overset{+}{C}HCl_2 > \overset{+}{C}H_2Cl$ or $\overset{+}{C}H_3$. Consequently, the yields of meta-nitrotoluene increase in the successive nitrations as noted in the preceding table. In equivalent terms, the concentrations, or reactivities, of the electromers of the opposite type, $\overset{-}{C_6H_5}\ \overset{+}{X}$, in the successive nitrations (1, 2, 3, and 4) are related as follows:—

$$\overset{-}{C_6H_5} . \overset{+}{CH_3} \text{ or } \overset{-}{C_6H_5}\ \overset{+}{CH_2Cl} > \overset{-}{C_6H_5}\ \overset{+}{CHCl_2} > \overset{-}{C_6H_5} . \overset{+}{CCl_3}$$

The conception of polar stability as heretofore applied to substituents or radicals does not lend itself to mathematical definition, but there may be assigned to a given substituent a *polar number* which may be defined as the algebraical sum of the positive and negative valences of that atom of the substituent or radical which is united to the benzene nucleus. Since a given substituent may function either positively or negatively, there shall not be included in this polar number the positive or the negative valence which unites the radical to the nucleus. According to this definition, the polar numbers of the radicals CH_3, CH_2Cl, $CHCl_2$, and CCl_3 appear from their electronic formulæ—

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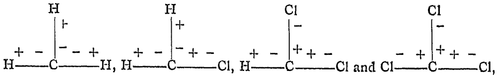


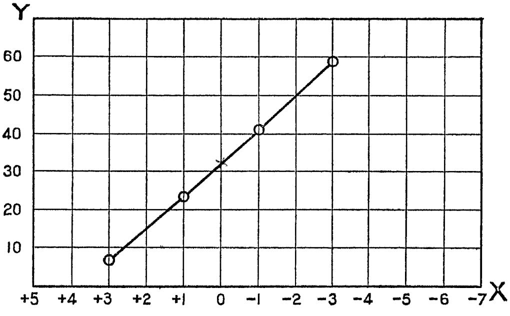
$H\overset{+\ -}{—}\overset{H}{C}\overset{-\ +}{—}H$, $H\overset{+\ -}{—}\overset{H}{C}\overset{-\ +\ -}{—}Cl$, $H\overset{+\ -}{—}\overset{Cl}{C}\overset{+\ +\ -}{—}Cl$ and $Cl\overset{-\ +}{—}\overset{Cl}{C}\overset{+\ +\ -}{—}Cl$,

to be, respectively, − 3, − 1, + 1, and + 3.

A remarkable relationship is found to exist between these polar numbers and the quantitative yields of the ortho-nitro-derivatives In the following table, the first column embodies the formulæ of the benzene derivatives, C_6H_5X, subjected to nitration The second column gives the polar number of the substituent X, and the third column contains the corresponding percentage yields of the ortho-nitro-derivative —

$C_6H_5\ X$	Polar Number of Substituent X	Ortho nitro derivative
$C_6H_5\ CH_3$	− 3	58·8
$C_6H_5\ CH_2Cl$	− 1	40·9
$C_6H_5\ CHCl_2$	+ 1	23·3
$C_6H_5 . CCl_3$	+ 3	6·8

If, in the system of rectangular co-ordinates, the polar numbers of the substituent (X) are indicated on the X axis and the corresponding percentage yields of the ortho-nitro-derivatives are indicated on the Y axis,



it is quite evident that the quantitative yields of the ortho-nitro-substitution products of toluene, benzyl chloride, benzal chloride, and benzotrichloride are a direct linear function of the polar numbers of the respective mono-substituents, CH_3, CH_2Cl, $CHCl_2$, and CCl_3 present in the nucleus. In the same manner (rectangular co-ordinates) it follows that the combined yields of the ortho- and para-nitrotoluenes on the one hand, or the yields of the meta-nitrotoluene on the other hand, are also linear functions of the polar numbers of the substituents CH_2Cl, $CHCl_2$ and CCl_3.

The existence of the foregoing relationships warrants a search for other quantitative relationships. To this end, the only quantitative data available are chiefly those of Holleman and his co-workers, who have carefully determined the yields (in per cent.) of the products of nitration of various mono-substituted derivatives of benzene. The nitration reactions were conducted so as to yield only mono-nitro-derivatives, ortho-, meta-, and para-. All the available data are embodied in the following table —

I Substituent (X) in Nucleus	II Polar Number	III Ortho	IV Para	V $(o + p)$	VI Meta
CH_3	-3	56·0	40·9	96·9	3·1
CH_2Cl	-1	40·9	54·9	95·8	4·2
F	0	12·4	87·6	100·0	0·0
Cl	0	30·1	69·9	100·0	0·0
Br	0	37·6	62·4	100·0	0·0
I	0	41·1	58·7	100·0	0·0
$CHCl_2$	$+1$	23·3	42·9	66·2	33·8
CCl_3	$+3$	6·8	28·7	35·5	64·5
$CO_2C_2H_5$	$+3$	28·3	3·3	31·6	68·4
CO_2CH_3	$+3$	21·0	5·8	26·8	73·2
CO_2H	$+3$	18·5	1·2	19·7	80·3
NO_2	$+4$	6·8	0·0	6·8	93·2

Column I embodies the formulæ of the substituents (X) of the mono-substituted derivatives C_6H_5X. The polar numbers of these substituents are indicated in column II. Columns III, IV, and VI embody the percentage yields of the ortho-, para-, and meta-nitro-compounds, respectively, of general formula $C_6H_4 . X . NO_2$. In column V the sum of the percentage yields of the ortho- and para-isomers is given. The data of the table have been tabulated in the order of the increasing values of the polar numbers of the substituents, i.e., from -3 to $+4$. This arrangement reveals some striking regularities which may be summarized as follows —

(1) When the polar number of a given substituent is zero or less than zero the combined yields of the ortho- and para-nitro-compounds range between ninety and one hundred per cent. In other words, the ortho-para type of substitution and percentage yield of products predominate practically to the exclusion of the meta type of substitution and yield when the polar number of the substituent in the nucleus is zero or less than zero.

(2) As the polar number assumes a positive sign and increases in value, the corresponding ortho-para percentage yield decreases while the meta yield increases. Thus when the polar number is + 4 the meta type of substitution and yield predominate almost to the exclusion of the ortho-para type and yield.

(3) From (1) and (2) it appears that the combined yields of the ortho- and para-nitro-substitution products and the yield of the meta-nitro-substitution product are predetermined, within certain limits, by the polar number of the substituent X in C_6H_5X. Therefore, if the yields of the ortho- and para-derivatives are dependent upon the speed of interaction of the electromer of the type $\overset{+}{C_6H_5}\ \overset{-}{X}$ and the yield of the meta-derivative depends upon the speed of the interaction of the electromer of the type $\overset{-}{C_6H_5}\,.\,\overset{+}{X}$ in the tautomeric system $\overset{+}{C_6H_5}\ \overset{-}{X} \rightleftharpoons \overset{-}{C_6H_5}\ \overset{+}{X}$, then it follows that *the speed of the interaction of these electromers with the substituting reagent is a function of the polar number of the substituent X in C_6H_5 X.* Furthermore, if the speeds of reaction of the electromers are dependent upon their concentration, then *these concentrations are also a function of the polar number of the substituents*.

(4) Finally, it should be noted that, in terms of positive and negative valences, the polar number of a substituent is in reality *an index of the degree or state of oxidation of that atom of the substituent which is directly united to the benzene nucleus*. This is in harmony with the principle that the development of positive valences (i e., loss of electrons) corresponds to oxidation while the development of negative valences (i e, gain of electrons) corresponds to reduction. In other words the problem of benzene substitution appears to be resolving itself into a study of the states of oxidation or reduction of the atoms of the substituents, i e, that atom of the substituent which is in direct combination with a carbon atom of the benzene nucleus. It is

significantly interesting to recall, indirectly in this connection, that the empirical rule of Brown and Gibson was based upon the susceptibility to oxidation of certain compounds. The significance of this feature was interpreted in the further analysis of the Brown and Gibson rule (Section B, Chapter IX).

The present chapter has indicated the existence of a relationship between the polar number of the substituent X in C_6H_5X, and the combined quantitative yields of the ortho- and para-mono-nitro-substitution products on the one hand, and the quantitative yield of the meta-nitro-derivative on the other There yet remains to be developed a relationship between the variable quantitative yields of the ortho- and the para-mono-nitro-substitution products, and the respective electronic formulæ of these products Perhaps a solution to this problem may also be found in a further development of the conception of the polar numbers of the substituents

CHAPTER XV

HALOGEN SUBSTITUTION IN THE BENZENE NUCLEUS AND IN THE SIDE-CHAIN.

SUBSTITUTION in the benzene nucleus has been considered at length in the preceding Chapters IX. to XIV, inclusive, with the special purpose of (1) explaining the types of substitution and (2) indicating the possibility of predicting the relative amounts (quantitative yields) of the various isomeric products obtained in substitution reactions Another interesting problem is presented in the action of halogens upon benzene derivatives containing side-chains In such reactions the halogen atoms may be substituted *either in the benzene nucleus or in the side-chains* Temperature, catalysts, such as *halogen-carriers*, and the photochemical action of light are the conditions which play prominent but perplexing parts in these complex substitution reactions

In view of the many phases of this problem, the present chapter is limited to a discussion and an interpretation chiefly of the action of bromine upon toluene There are two very evident reasons for this (1) Toluene is the simplest derivative of benzene which may be regarded as possessing a side-chain, or, perhaps more correctly, a radical, the hydrogen atoms of which are comparable in their chemical behaviour with the hydrogen atoms of side-chains containing more than one carbon atom (2) Practically all of the research relating to the problem of substitution in the benzene nucleus and in the side-chain has been confined to the action, under various conditions, of chlorine and bromine upon toluene

A comprehensive idea of the nature and extent of the work upon this subject has been presented by Bancroft from the standpoint of "halogen-carriers" and the electrochemistry of light [86] The general conclusions, briefly indicated, are as follows Toluene undergoes substitution either in the nucleus or in the side-chain according to the conditions. Schramm [87] found that chlorine or bromine substitutes the hydrogen atoms of the side-chain, at 0°, and at higher temperatures, *in the sunlight* In diffused daylight and in the dark a mixture of ortho- and para-, chloro- and bromo-toluene results, and a like effect is produced among the higher homologues Cannizzaro[88] observed that side-chain substitution took place in the dark at the boiling-point of toluene On the other hand, nucleus substitution is induced by the usual carriers, such as ferric chloride, molybdenum, and antimony pentachloride, iodine chloride, pyridine, and the aluminium-mercury couple The most recent and noteworthy contribution is the work of Cohen, Dawson, Blockey, and Woodmansey,[89] who found that, at the boiling-point of toluene, moist chlorine in the dark produces nuclear substitution to the extent of nearly 90 per cent, whereas in the light, dry chlorine increases side-chain substitution, yielding on the average about 94 per cent of benzyl chloride Furthermore, they make this statement "In so far as the resultant effects are concerned, the action of moisture is opposed to that of light, for this increases the rate of side-chain substitution, and the former accelerates the rate of nuclear substitution".

Various explanations have been proposed to account for these remarkable phenomena Especially noteworthy are those of Bruner,[90] Bancroft,[91] and Holleman[92] The fundamental features of these explanations should be noted briefly, since they are to be reconsidered from the electronic standpoint of valence

Bruner maintains that side-chain substitution is due to molecular halogen, while nucleus substitution is effected by halogen atoms or ions, which result from the dissociation of the halogen molecules The velocity measurements of Bruner and Dluska favour this hypothesis, since both side-chain and nucleus substitution processes apparently take place according to the requirements of the equation for a unimolecular change, if the concentration of the bromine is small. For higher concentrations of bromine the values obtained for the unimolecular constant decrease as the reaction proceeds This is attributed to the removal of the active bromine from the solution by the formation of a perbromide (HBr_3)

Bruner's idea that nucleus substitution is due to ionic bromine is also maintained by Bancroft, who further assumes that nuclear substitution occurs when *negative* bromine ions are present in excess of the positive bromine ions. This condition is brought about presumably by the partial combination of positive bromine ions with molecular bromine to form complex positive ions, thus —

$$Br_2 = Br^+ + Br^- , \quad Br_2 + Br^+ \rightarrow Br_2 Br^+$$

On the other hand, Bancroft maintains that side-chain substitution takes place under conditions which tend to yield a preponderance of positive bromine ions.

Holleman assumes that side-chain substitution is due to molecular bromine, while nucleus substitution is brought about by a perbromide, HBr_n. The formation of these polyhalogen compounds is actually favoured by low temperature and increasing concentration of solution, and these are the conditions which also favour nucleus substitution.

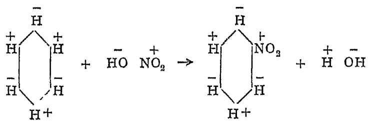
Notwithstanding the various explanations that have been proposed to account for the remarkable phenomena encountered in nucleus and in side-chain substitution, Cohen frankly states,[93] "*it must be confessed that nothing definite is known about the mechanism of the process*". In this connection, it may be of interest to recall a statement made by Brown and Gibson when they formulated a rule for determining whether a given benzene mono-derivative will give chiefly a meta-di-derivative or a mixture of ortho- and para-di-derivatives. They stated that their rule is not a law, because "it has no visible relation to any *mechanism* by which substitution is carried out in one way, rather than in another way," but, since they found it capable of most rigorous application, they concluded that "it must be related in some way to a law, and may be of use in guiding us to the cause of the formation of meta-compounds in some cases, and of ortho and para in others". Now the application of the electronic conception of positive and negative valences to the constituent atoms of the benzene molecule and to the principles of the Brown and Gibson rule, not only rendered possible an interpretation of the rule, but also indicated a *mechanism* according to which substitution must take place in one way rather than in another way. This was a consequence of the evidence, both theoretical and experimental, that in benzene the hydrogen atoms in positions 1, 3, and 5 are negative, while the hydrogen atoms in positions 2, 4, and 6 (relatively speaking) are positive. Accordingly, when substituents are of the same sign or polarity they occupy positions which are meta to each other, but if two substituents are of opposite sign or polarity they will occupy positions either ortho or para to each other. The extension of these principles, and the electronic conception of valence to the *phenomena* and *conditions* of nucleus and side-chain substitution may afford not only an explanation of the phenomena, but also indicate a possible and a probable mechanism of the process

A. Nucleus Substitution in Toluene.

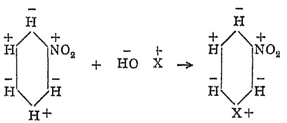
Any interpretation of the action of the halogens upon toluene, under the various conditions just noted, must take into account the following facts (1) The presence of water (moisture), (2) low temperature, (3) the absence of sunlight (subdued daylight or darkness), and (4) the presence of halogen carriers, all favour nucleus substitution with the consequent formation of *o*- and *p*-chloro- or bromotoluenes. On the other hand, the elimination of water, higher temperatures, and sunlight are the conditions which favour side-chain substitution.

Omitting, temporarily, the discussion of the action of halogen carriers, it is quite important to note that the conditions (1), (2), and (3) which favour substitution in the nucleus are the very conditions which promote the formation, and conserve the stability of, hypochlorous and hypobromous acids (HOX) in which the halogen (X) functions positively. On the other hand, the conditions which favour side-chain substitution, namely, heat, light, and the absence of water, are those which render hypochlorous and hypobromous acids unstable and promote their action as oxidizing agents These facts are now to be interpreted as warranting the assumption that substitution in the nucleus in the presence of water (even in minutest traces) is favoured by the intermediate formation of hypochlorous or hypobromous acids which on interaction with toluene effect *nucleus substitution of positive halogen*

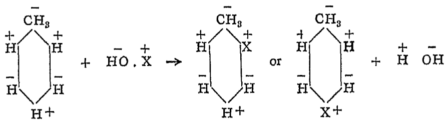
It should be recalled, in this connection, that substituted halogen may function sometimes positively, sometimes negatively. For instance, in *o*- and *p*-chloro- or bromonitrobenzene the halogen atoms are negative, since they are exchanged for negative hydroxyl in double decomposition reactions with aqueous potassium hydroxide ($\overset{+}{K}.\overset{-}{OH}$) On the other hand, the halogen atoms in the *m*-nitro-compounds are regarded as positive for the following reasons First, the halogen atom is not exchangeable for negative hydroxyl Second, it is in the meta position to the positive nitro-radical, and, according to the electronic formula of benzene, those substituents which are meta to each other are of the same sign or polarity. Third, the substitution of halogen in the nucleus is facilitated if the reagents are not anhydrous This indicates the possibility of the intermediate formation of the hydroxy-halogen acid (HO X) in which the halogen (X) is positive Accordingly, the electronic equations for the formation of *m*-chloro- and *m*-bromonitrobenzene are represented as follows —



$$X_2 = \overset{+}{X}—\overset{-}{X} + \overset{+}{H}—\overset{-\ -}{O}—\overset{+}{H} \rightarrow \overset{+}{H}—\overset{-}{X} + \overset{+}{H}—\overset{-\ -}{O}—\overset{+}{X}$$



The substitution of positive halogen in toluene proceeds in the same way, but here the halogen assumes the ortho or the para position with respect to the negative methyl radical as follows —

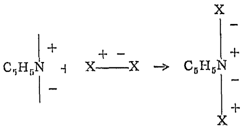


Further evidence of the positive character of the nucleus substituted halogen of toluene is shown by an application of the electronic conception of valence to the Brown and Gibson rule from which standpoint toluene is a derivative of $\overset{+}{H}\ \overset{-}{CH_3}$ and not $\overset{-}{HO}\ \overset{+}{CH_3}$. Hence substituents ortho or para to the negative methyl radical must be positive. Moreover, the substituted halogen atoms are not directly exchangeable for negative hydroxyl and hence are regarded as positive.

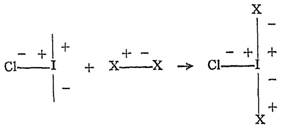
The above conclusions are directly opposed to the assumption of Bancroft that nucleus substitution is due to negative halogen. The work of Cohen, showing that moisture increases both the rate and extent of nucleus substitution, also contradicts Bancroft's assumption, if we admit the interaction of the intermediately produced hydroxy-halogen acid ($\overset{-}{HO}\ \overset{+}{X}$) upon toluene according to the above electronic formulæ and equations.

B. The Action of Halogen Carriers.

Since water increases both the rate and extent of nucleus substitution, is it not reasonable to regard water as a halogen carrier? This point of view may throw some light upon the action of halogen carriers in general in effecting nucleus substitution. For instance, pyridine and iodine chloride may be compared to water in that each contains an unsaturated atom which renders possible the formation of addition compounds as follows —



$$C_5H_5N + \overset{+}{X}\!-\!\overset{-}{X} \rightarrow C_5H_5N\begin{smallmatrix}X\\X\end{smallmatrix}$$



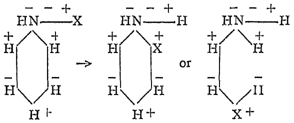
$$\overset{-}{Cl}\!-\!\overset{+}{I} + \overset{+}{X}\!-\!\overset{-}{X} \rightarrow Cl\!-\!I\begin{smallmatrix}X\\X\end{smallmatrix}$$

Either of these halogen addition-compounds may dissociate in two ways. Consider the pyridine compound:—

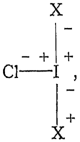
$$(1)\ C_5H_5\overset{+}{N}\overset{-}{X}X \rightarrow C_5H_5N\overset{-}{X} + \overset{+}{X}$$

$$(2)\ C_5H_5\overset{+}{N}\overset{-}{X}X \rightarrow C_5H_5N\overset{+}{X} + \overset{-}{X}$$

The previously presented evidence favours dissociation according to equation (1) since it would account for the nucleus substitution of positive halogen Further evidence is afforded from the standpoint of a comparison of the relative stability of the nitrogen halogen linkings in the halogen addition compounds The pyridine halogen compound shows the linkings $(\overset{-}{N}—\overset{+}{X})$ and $(\overset{+}{N}—X)$ The former linking is presumably the least stable and therefore more likely to undergo dissociation, yielding positive halogen This assumption is warranted by the extreme instability of compounds embodying this linking For example, W A Noyes [91] first showed that the halogen atoms in nitrogen trichloride were positive and bound to negative nitrogen valences This compound is extremely unstable The substituted nitrogen halides also embody the linkings $(\overset{-}{N}—\overset{+}{X})$ and are likewise very unstable, exchanging the positive halogen atom for positive hydrogen of the nucleus thereby developing a more stable linking $(\overset{-}{N}—\overset{+}{H})$ thus —



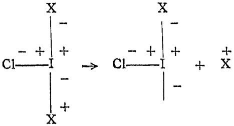
On the other hand, the compounds nitrosyl chloride and bromide of the formula $\overset{-}{\underset{-}{O}}=\overset{+}{\underset{+}{N}}\overset{+}{—}\overset{-}{X}$ embody the linking $(\overset{+}{N}—\overset{-}{X})$ and are very stable in comparison with the previously noted compounds containing the $(\overset{-}{N}—\overset{+}{X})$ linking



Considering the other typical halogen carrier, $\begin{array}{c} X \\ |\,- \\ Cl\overset{-\ +}{—}\overset{+}{I} \\ |\,- \\ |\,+ \\ X \end{array}$, it appears that the linking $(\overset{+}{\mathrm{I}}\text{——}\overset{-}{\mathrm{X}})$ is more stable than $(\overset{-}{\mathrm{I}}\text{——}\overset{+}{\mathrm{X}})$ This is substantiated by the fact that iodine in iodine chloride and in iodine bromide is positive as evidenced by its interaction with potassium hydroxide, yielding potassium hypoiodite in which the iodine is positive —

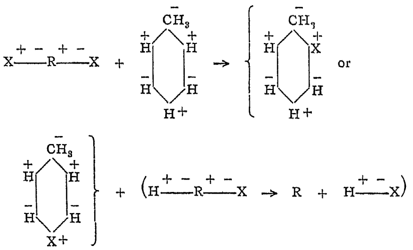
$$\overset{+}{\mathrm{I}}\text{——}\overset{-}{\mathrm{X}} + 2\overset{+}{\mathrm{K}}\text{——}\overset{-\ -}{\mathrm{O}}\text{——}\overset{+}{\mathrm{H}} \rightarrow \overset{+}{\mathrm{K}}\text{——}\overset{-\ -}{\mathrm{O}}\text{——}\overset{+}{\mathrm{I}} + \overset{+}{\mathrm{K}}\text{——}\overset{-}{\mathrm{X}} + \overset{+}{\mathrm{H}}\text{——}\overset{-\ -}{\mathrm{O}}\text{——}\overset{+}{\mathrm{H}}$$

Accordingly, the halogen addition compound would maintain the more stable linking, $\overset{+}{\mathrm{I}}\text{——}\overset{-}{\mathrm{X}}$, and yield the positive halogen ion as follows —



From the above points of view the following mechanism, or cycle of changes, will illustrate the part played by the halogen carrier in effecting the nucleus substitution of positive halogen in toluene R represents any halogen carrier such as water, pyridine, iodine chloride, phosphorus-, antimony-, and molybdenum-trihalides, or any other compound containing an atom which in uniting with chlorine or bromine, X_2, increases its valence from (n) to $(n + 2)$ as follows —

$$\mathrm{R} + \overset{+}{\mathrm{X}}\text{——}\overset{-}{\mathrm{X}} \rightarrow \overset{+}{\mathrm{X}}\text{——}\overset{-\ +}{\mathrm{R}}\text{——}\overset{-}{\mathrm{X}}$$



$$\left(\overset{+}{\mathrm{H}}\text{——}\overset{-\ +}{\mathrm{R}}\text{——}\overset{-}{\mathrm{X}} \rightarrow \mathrm{R} + \overset{+}{\mathrm{H}}\text{——}\overset{-}{\mathrm{X}}\right)$$

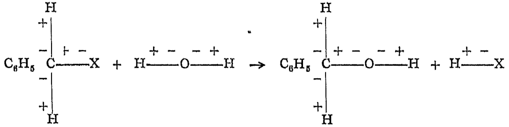
It should be observed that the halogen acid eliminated during the course of the substitution is of the type $\overset{+}{\text{H}}\text{——}\overset{-}{\text{X}}$, and not $\overset{-}{\text{H}}\text{——}\overset{+}{\text{X}}$, the latter electromer never having been identified. If neither oxidation nor reduction has occurred during nucleus substitution then the elimination of $\overset{+}{\text{H}}\text{——}\overset{-}{\text{X}}$ is conclusive evidence that the substituted halogen atom is positive, the reaction having proceeded as indicated above. Halogen carriers of other types may function similarly, i.e., substitute positive halogen and eliminate $\overset{+}{\text{H}}\text{——}\overset{-}{\text{X}}$.

Any halide functioning as a halogen carrier may conform to the above scheme since its halogen atom may be unsaturated and hence combine with other halogen atoms just as the iodine atom in iodine chloride lends itself to the formation of iodine trichloride.

C. Side-Chain Substitution.

In what respects does side-chain substitution differ from nucleus substitution? It has just been shown that nucleus substitution of toluene yields ortho- and para-halogen substituted toluenes in which the halogen is positive, but when side-chain substitution takes place experimental evidence shows that the substituted halogen atoms are negative. This evidence is as follows:—

Benzyl chloride, benzal chloride, and benzotrichloride (or bromides) are readily hydrolyzed by water or by potassium hydroxide, yielding, respectively, benzyl alcohol, benzaldehyde, and benzoic acids. In each of these hydrolyses, chlorine (or bromine) is replaced by negative hydroxyl, which signifies that the substituted halogen atoms of the side-chain are negative. The reaction for the hydrolysis of benzyl chloride, or bromide, is typical and may be represented by the following equation:—

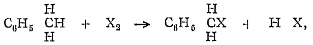


$$C_6H_5\,\begin{array}{c}\text{H}\\ +\vert\\ -\vert\\ \text{C}\\ -\vert\\ +\vert\\ \text{H}\end{array}\overset{+\ \ -}{\text{——}}\text{X} + \text{H}\overset{+\ \ -}{\text{——}}\text{O}\overset{-\ \ +}{\text{——}}\text{H} \rightarrow C_6H_5\,\begin{array}{c}\text{H}\\ +\vert\\ -\vert\\ \text{C}\\ -\vert\\ +\vert\\ \text{H}\end{array}\overset{+\ \ -}{\text{——}}\text{O}\overset{-\ \ +}{\text{——}}\text{H} + \text{H}\overset{+\ \ -}{\text{——}}\text{X}$$

This reaction may be reversed by the action of hydrogen halide $(\overset{+}{H}\text{——}\overset{-}{X})$ which converts benzyl alcohol into benzyl halide. This also establishes the fact that halogen atoms substituted in the side-chain are negative. An interpretation of these facts must correlate the electronic conception of positive and negative valences with the conditions under which side-chain substitution takes place.

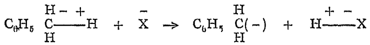
The most significant feature to be noted is that in nucleus substitution the positive hydrogen atoms of toluene are replaced by positive halogen atoms, which change involves neither oxidation nor reduction. But in side-chain substitution, positive hydrogen atoms are replaced by halogen atoms which function negatively. In other words, side-chain substitution involves oxidation and reduction since the carbon-hydrogen linking $(\overset{-}{C}\text{——}\overset{+}{H})$ is changed to a carbon-halogen linking $(\overset{+}{C}\text{——}\overset{-}{X})$. The negative valence of carbon is oxidized to a positive valence and this change could not occur unless the substituting agent is reduced.

The side-chain substitution reaction, generally represented by the equation—



$$C_6H_5\,\underset{H}{\overset{H}{C}}H + X_2 \rightarrow C_6H_5\,\underset{H}{\overset{H}{C}}X + H\,X,$$

will now be analysed so as to indicate clearly the oxidation-reduction phases of the change. (1) The substituting reagent, molecular halogen, dissociates yielding positive and negative halogen atoms, $X_2 \rightleftharpoons \overset{+}{X} + \overset{-}{X}$. (2) The negative halogen atom unites with a positive hydrogen atom of the side-chain—



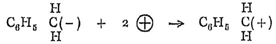
$$C_6H_5\,\underset{H}{\overset{H\ -}{C}}\text{——}\overset{+}{H} + \overset{-}{X} \rightarrow C_6H_5\,\underset{H}{\overset{H}{C}}(-) + \overset{+}{H}\text{——}\overset{-}{X}$$

(3) The positive halogen atom, *under the conditions which effect side-chain substitution*, tends to become negative and thereby is reduced. In other words, it acts as an oxidizing agent according to either of the equivalent schemes, (*a*) or (*b*):—

$$(a)\ \overset{+}{X} \rightarrow \overset{-}{X} + 2\oplus$$

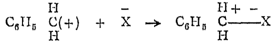
$$(b)\ \overset{+}{X} + 2\ominus \rightarrow \overset{-}{X}$$

(4) This conversion of $\overset{+}{X}$ to $\overset{-}{X}$ is accompanied by an oxidation of the negative valence of the carbon atom of the side chain to a positive valence—



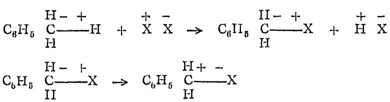
$$C_6H_5\,\overset{H}{\underset{H}{C}}(-) + 2\oplus \rightarrow C_6H_5\,\overset{H}{\underset{H}{C}}(+)$$

(5) The resultant positive valence of the carbon atom then "binds" the negative halogen atom, $\overset{-}{X}$:—



$$C_6H_5\,\overset{H}{\underset{H}{C}}(+) + \overset{-}{X} \rightarrow C_6H_5\,\overset{H+\ -}{\underset{H}{C\text{——}X}}$$

The preceding analysis of side-chain substitution may be summarized briefly as an intramolecular oxidation-reduction process:—



$$(1)\ C_6H_5\,\overset{H-\ +}{\underset{H}{C\text{——}H}} + \overset{+\ -}{X\ X} \rightarrow C_6H_5\,\overset{H-\ +}{\underset{H}{C\text{——}X}} + \overset{+\ -}{H\ X}$$

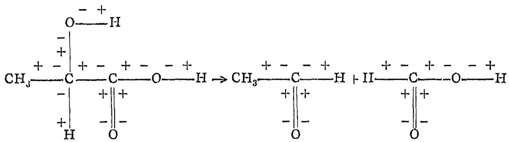
$$(2)\ C_6H_5\,\overset{H-\ +}{\underset{H}{C\text{——}X}} \rightarrow C_6H_5\,\overset{H+\ -}{\underset{H}{C\text{——}X}}$$

Equation (1) shows the substitution of a positive halogen atom in the side chain forming an electromer containing the carbon-halogen linking ($\overset{-\ \ +}{C\text{——}X}$), but *under the conditions which effect side-chain substitution*, the electromer $C_6H_5\,\overset{H-\ +}{\underset{H}{C\text{——}X}}$ is transformed by intramolecular oxidation-reduction to the electromer $C_6H_5\,\overset{H+\ -}{\underset{H}{C\text{——}X}}$ which embodies the carbon-halogen linking ($\overset{+\ \ -}{C\text{——}X}$) Thus it is evident that both of the proposed interpretations are in the end electronically identical The remaining hydrogen atoms of the side-chain undergo substitution in the same manner

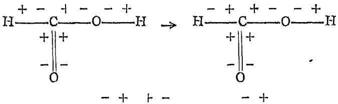
Having indicated an oxidation-reduction mechanism which accounts for the substitution of negative halogen in the side-chain, it is now desirable to account for the fact that *nucleus substitution does not involve oxidation while side-chain substitution does*

It has been observed that the conditions which promote nucleus substitution (omitting halogen carriers which have been considered) are low temperature and the absence of sunlight. These are the conditions which promote the formation and conserve the stability of hypochlorous and hypobromous acids, that is, prevent their decomposition as oxidizing agents. On the other hand, the chief conditions promoting side-chain substitution (heat and sunlight) are the very factors which render these hydroxy-halogen acids unstable and promote their action as oxidizing agents. Let us now inquire into the most significant feature of these changes. If hypochlorous or hypobromous acids are heated or exposed to the action of sunlight, oxygen is evolved and hydrogen chloride or bromide is formed ($2HOX \rightarrow 2HX + O_2$). The halogen in HOX is positive, in HX it is negative. Hence it follows that heat, and especially *the photochemical action of light, effect the conversion of positive halogen to negative halogen, thus,* $\overset{+}{X} \rightarrow \overset{-}{X} + 2\oplus$. This is the oxidation process upon which the elimination of oxygen from HOX depends. Now the substitution of halogen in the side-chain, as described above, is also an oxidation process, since it likewise involves the essential change, $\overset{+}{X} \rightarrow \overset{-}{X} + 2\oplus$, induced either by heat or by photochemical action. Thus the conditions which favour and promote side-chain substitution are correlated with the fact that positive hydrogen atoms of the side-chain are eventually substituted by negative halogen atoms, which change involves the reduction of positive halogen to negative halogen, and the concomitant oxidation of negative valences of the carbon atom of the side-chain to positive valences. These bind the negative halogen atoms.

In this connection it may be of interest to note and to correlate another of many reactions in which light changes negative valences of carbon to positive valences. Euler and Ryd[95] have shown that lactic acid under the influence of ultraviolet rays evolves carbon dioxide. The electronic interpretation depends upon the fact that lactic acid readily yields aldehyde and formic acid as follows —



Now in order that formic acid, in which three of the carbon valences are positive, and one is negative, may yield carbon dioxide, in which the four valences of carbon are positive, the one negative valence of carbon in formic acid must be oxidized to a positive valence This change takes place when formic acid is catalytically or photochemically decomposed, yielding carbon dioxide and hydrogen according to the following electronic equation —



Here also the photochemical change is an intramolecular oxidation-reduction reaction, the electromer $H\overset{+\ \ -}{\text{——}}CO_2H$ is transformed to the electromer $H\overset{-\ \ +}{\text{——}}CO_2H$. Then decomposition into carbon dioxide and hydrogen is possible and takes place

In this chapter some fundamental distinctions between nucleus and side-chain substitution have been developed and interpreted in terms of positive and negative valences. A common occurrence, however, should not be overlooked, namely, that in most substitution reactions it is practically impossible so to limit and regulate the conditions that the *sole* reaction taking place will be either nucleus substitution or side-chain substitution. In other words, the formation of ortho- and para-halogen substituted toluenes, in which the halogen atoms are positive, and the introduction of negative halogen into the side-chain, may proceed as simultaneous independent chemical changes. As previously noted the former process does not involve oxidation and reduction while the latter does. These facts are readily correlated with another general property characteristic of benzene on the one hand, and characteristic of aliphatic hydrocarbons (comparable to side-chains) on the other hand. *Benzene resists oxidation, while the aliphatic hydrocarbons and the side-chains are generally more susceptible to oxidation*

Finally, it is not impossible to conceive that, under certain conditions, which are not as yet determined and interpreted, a positive hydrogen atom of the benzene nucleus may be replaced by a negative halogen atom (or vice versâ), which is characteristic of side-chain substitution, involving oxidation and reduction Such a condition, however, does not invalidate the interpretations presented in this paper, which are correlated with the experimental facts, the conditions of substitution, and the chemical properties of ortho- and para-halogen substituted toluenes, and the side-chain substitution products

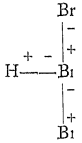
In concluding this chapter, the relations between the electronic interpretations and the substitution hypotheses of Bruner, Bancroft, and Holleman should be reconsidered briefly

Bruner's idea that nucleus substitution is due to halogen atoms, while side-chain substitution is due to molecules, thus,

$$C_6H_5CH_3 + 2Br \rightarrow BrC_6H_4CH_3 + HBr,$$
$$C_6H_5CH_3 + Br_2 \rightarrow C_6H_5CH_2Br + HBr,$$

fails to take into account the fact that nucleus substitution (former equation) does not involve oxidation and reduction, while side-chain substitution (latter equation) does

Bancroft's assumption that nucleus substitution is due to negative halogen atoms is not in agreement with the evidence, both theoretical and experimental, that the ortho- and para-substituted halogen atoms of toluene are positive His other assumption that the halogen substituted in the side-chain is positive is also contradicted by the fact that the halogen atoms in benzyl chloride, benzal chloride, and benzotrichloride (or bromides) are negative, since they are readily exchanged (without oxidation or reduction) for negative hydroxyl It is true, however, that positive halogen atoms are the active substituting agents in side-chain substitution, but only by virtue of their oxidizing action and consequent reduction to negative halogen (photochemical action) as previously described

Finally, Holleman has stated « Il est démontré, que l'hypothèse, suivant laquelle le noyau est attaqué par des molécules HBr_n, tandis que la chaîne latérale l'est par les molécules de brome, a quelque vraisemblance, cependant un nombre de difficultés doivent encore être levées, avant qu'elle puisse servir à expliquer les phénomènes observés" The very plausible interpretation of the nucleus bromination of toluene through the action of the intermediately formed HBr_n, may be readily correlated with the interpretation of nucleus substitution, and the action of halogen carriers as presented in this chapter, provided HBr_n, be regarded as  $$\begin{array}{ccc} & & Br \\ & & \big|{\scriptstyle -} \\ & & \big|{\scriptstyle +} \\ \overset{+}{H} & \overset{-}{\text{——}} & Br \\ & & \big|{\scriptstyle -} \\ & & \big|{\scriptstyle +} \\ & & Br \end{array}$$ But Holleman's idea of side-chain substitution is subject to the criticism that it also fails to recognize the side-chain substitution process as an oxidation and reduction phenomenon depending upon the reaction, $\overset{+}{X} \rightarrow \overset{-}{X} + 2\oplus$, previously considered

CHAPTER XVI

"FREE RADICALS": THEIR EXISTENCE AND PROPERTIES

RADICALS are conceived to be groups of atoms which function as single atoms in chemical reactions and, accordingly, preserve their composition or constitution throughout chemical changes. The history of Chemistry affords many instances of attempts to isolate radicals, i.e., to prepare "free radicals." As early as 1834 Liebig[96] suggested the possibility of isolating, and seriously attempted to prepare, free radicals. In 1839 Lowig[97] claimed to have effected the separation of the radical ethyl, C_2H_5. An historical review of these various attempts, chiefly failures, would constitute an interesting chapter, the culmination of which, however, is found in the recent work of Gomberg,[98] who, undoubtedly, has isolated free radicals, notably in the form of the triarylmethyls.

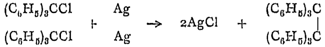
The triarylmethyls are regarded by many to be compounds of tervalent carbon. Schlenck's discoveries,[99] by means of molecular weight determinations, that some of the triarylmethyls are largely mono-molecular (for instance, tri-*bi*-phenylmethyl was found to be entirely mono-molecular) leads, as Gomberg has emphasized, to but one inference, namely, that these compounds exist as free radicals, i.e., they are compounds of the tervalent carbon atom of the general formula $(R)_3 \equiv C$.

The present chapter offers an interpretation of the existence and properties of free radicals in terms of the electronic conception of positive and negative valences which reveals the existence of many significant relationships that are apparent in electronic formulæ but that cannot be found in ordinary structural formulæ. The principles developed in Chapter IV, Electronic Amphoterism, and especially those of Chapter V, The Nascent State, are both essential and fundamental to an appreciation of the interpretations presented in this chapter.

Particular attention should be redirected to the fact that all the chemical actions classed as "nascent" are of a reduction or an oxidation type, and that the so-called "nascent state" is conceived to be *an unstable condition of a substance which manifests (under certain conditions) an adaptibility and a tendency to lose electrons, or gain electrons, and thereby revert to a more stable condition If the substance (ion, atom, or molecule) loses negative electrons, it acts as a reducing agent If it combines with negative electrons, it acts as an oxidizing agent*

From the point of view embodied in the above definition, the present chapter will endeavour to show that *free radicals* such as the triarylmethyls, are comparable in many respects with the *electrically neutral atomic state*, and that their instability, or reactivity, and general chemical properties may be interpreted by their development of positive or of negative valences through the loss or gain, respectively, of negative electrons In other words, the triarylmethyls may act either as reducing or as oxidizing agents Furthermore, in explaining some of the rearrangement reactions peculiar to triphenylmethyl, the electronic formula of benzene will be shown to play a significant part

Consider, first, the reaction for the preparation of triphenylmethyl Gomberg[100] submitted triphenylchloromethane to the action of metals, notably silver, with the full expectation that the reaction would proceed normally and give rise to hexaphenylethane :—



$$\begin{array}{l} (C_6H_5)_3CCl \\ (C_6H_5)_3CCl \end{array} + \begin{array}{l} Ag \\ Ag \end{array} \rightarrow 2AgCl + \begin{array}{l} (C_6H_5)_3C \\ \quad\quad\quad\;| \\ (C_6H_5)_3C \end{array}$$

He obtained "a hydrocarbon possessing the requisite composition (C = 93 8 per cent, H = 6 2 per cent) But the unusual instability of this substance, its proneness to enter into the most varied chemical reactions, and above all, its striking unsaturated character, precluded the natural inference that the hydrocarbon at hand was actually hexaphenylethane The opinion was expressed that here was an instance of a compound with one atom of carbon in the trivalent state, i e., $(C_6H_5)_3C$, *triphenylmethyl*, a free radical" Now it may be shown that *the electronic interpretation of the action of silver upon triphenylchloromethane also substantiates the assumption of the existence of the free radical as a compound of tervalent carbon.*

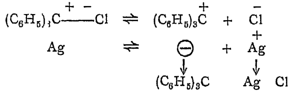
Triphenylchloromethane presumably possesses the abbreviated electronic formula[1] $(C_6H_5)_3C\overset{+\ -}{\text{——}}Cl$. Its aqueous solution is a conductor of the electric current depending upon ionic dissociation—

$$(C_6H_5)_3C\overset{+\ -}{\text{——}}Cl \rightleftharpoons (C_6H_5)_3\overset{+}{C} + \overset{-}{Cl}$$

Furthermore, its hydrolysis conforms to the equation

$$(C_6H_5)_3\overset{+}{C}\ \overset{-}{Cl} + \overset{+}{K}\ \overset{-}{OH} \rightarrow (C_6H_5)_3\overset{+}{C}\ \overset{-}{OH} + \overset{+}{K}\ \overset{-}{Cl}.$$

Metallic silver (with zero valence) in order to combine with negative chlorine, must itself develop a positive valence, i e, it must become positively univalent through the loss of an electron $Ag \rightarrow \ominus + \overset{+}{Ag}$ Accordingly, the electronic scheme for the action of silver upon triphenylmethylchloride is represented as follows —



$$\begin{array}{ccccc} (C_6H_5)_3C\overset{+\ -}{\text{——}}Cl & \rightleftharpoons & (C_6H_5)_3\overset{+}{C} & + & \overset{-}{Cl} \\ Ag & \rightleftharpoons & \ominus & + & \overset{+}{Ag} \\ & & \downarrow & & \downarrow \\ & & (C_6H_5)_3C & & Ag\ Cl \end{array}$$

It should be observed that the methyl carbon atom in the triphenylmethyl ion is quadrivalent, but the free positive valence of this ion is obliterated by the acquisition of the negative electron from the metallic silver In other words, silver has reduced the quadrivalent methyl carbon atom to the tervalent state, yielding triphenylmethyl

The possible reaction of two electrically neutral molecules of triphenylmethyl to form hexaphenylethane is exactly parallel to the reaction of two electrically neutral hydrogen atoms to form molecular hydrogen The reaction depends upon one of the atoms, or free radicals, losing an electron which is acquired by the other atom, or free radical, respectively. Combination of the resulting oppositely charged atoms or radicals occurs simultaneously as indicated in the following scheme:—

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[1] See the equally applicable "quinocarbonium formula" in a later section of this chapter, p 161

$$\left.\begin{array}{l} H \rightarrow \ominus + \overset{+}{H} \\ H + \ominus \rightarrow \overset{-}{H} \end{array}\right\} \rightarrow H\overset{+\ -}{\text{——}}H = H_2$$

$$\left.\begin{array}{l} (C_6H_5)_3C \rightarrow \ominus + (C_6H_5)_3\overset{+}{C} \\ (C_6H_5)_3C + \ominus \rightarrow (C_6H_5)_3\overset{-}{C} \end{array}\right\} \rightarrow (C_6H_5)_3C\overset{+\ -}{\text{——}}C(C_6H_5)_3$$

The following properties of triphenylmethyl will be considered. (A) oxidation, (B) addition of iodine, (C) addition of hydrogen, (D) reaction with nitrogen dioxide (or tetroxide), (E) addition of xylene, (F) action of acids, (G) action of light, (H) electrical conductivity of triphenylmethyl when dissolved in liquid sulphur dioxide, based upon the analogous conductivity of sodium dissolved in liquid ammonia

Gomberg has frequently called attention to the fact that triphenylmethyl behaves in some reactions as if it were an element of basic nature This is particularly so in its reactions with oxygen and with iodine This behaviour, from the electronic standpoint, may be attributed to the tendency of the tervalent carbon atom to become quadrivalent, i e, to develop a positive valence through the loss of an electron in just the same way that metallic silver or sodium develops a positive valence —

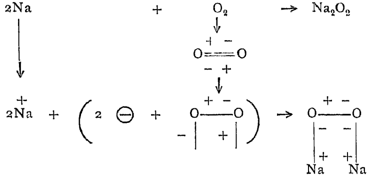
$$Na \rightarrow \overset{+}{Na} + \ominus$$

$$(C_6H_5)_3C \rightarrow (C_6H_5)_3\overset{+}{C} + \ominus.$$

The striking similarity of triphenylmethyl to sodium is shown in the reactions of each with (A) oxygen, and (B) iodine

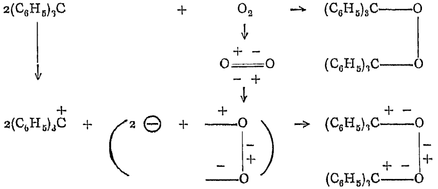
A. Oxidation

On exposure of a concentrated solution of triphenylmethyl in benzene (10 per cent.) to air, a colourless fairly stable peroxide, $\{(C_6H_5)_3C\}_2O_2$, is formed Sodium and oxygen combine at temperatures below 180° yielding a mixture of sodium oxide and peroxide As the temperature is raised the quantity of peroxide increases. At 300° sodium peroxide is the principal product Now metallic sodium possesses neither positive nor negative valences, but in its oxide and peroxide sodium is presumably positively univalent, since these oxides on hydrolysis yield sodium hydroxide, $\overset{+}{\mathrm{Na}}\ \overset{-}{\mathrm{OH}}$. Accordingly, the complete electronic scheme for the formation of sodium peroxide may be represented as follows :—



The parenthetical part of the scheme involves the reduction of a positive valence of oxygen to a negative valence by the action of the electrons from sodium. The sodium atoms, thus becoming positive, unite with the negative valences of the oxygen atoms.

In a perfectly analogous manner triphenylmethyl unites with oxygen, thus :—



B. Addition of Iodine.

The combination of either sodium or triphenylmethyl with iodine is also an oxidation-reduction reaction. Gomberg[101] has shown that triphenylmethyl may be titrated with a standard solution of iodine. Triphenylmethyliodide is formed. The iodine in this compound is negative since it is replaced by negative hydroxyl on hydrolysis. The iodine atom in sodium iodide is also negative since the aqueous solutions yield the ions $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{I}}$. Accordingly, the electronic schemes for the combinations of sodium and of triphenylmethyl with iodine (i.e., their oxidation by means of iodine) are represented as follows :—

$$\begin{tikzcd}
2\mathrm{Na} \arrow[dd] & + & \mathrm{I}_2 \arrow[d] & \rightarrow & 2\mathrm{NaI} \\
 & & \overset{+}{\mathrm{I}}\text{---}\overset{-}{\mathrm{I}} \arrow[d] & & \\
2\overset{+}{\mathrm{Na}} & + & (2\ominus + \overset{+}{\mathrm{I}} + \overset{-}{\mathrm{I}}) & \rightarrow & 2\overset{+}{\mathrm{Na}}\text{---}\overset{-}{\mathrm{I}}
\end{tikzcd}$$

In the parenthetical part of the scheme the electrons from sodium reduce $\overset{+}{\mathrm{I}}$ to $\overset{-}{\mathrm{I}}$. In the following scheme the electrons from triphenylmethyl accomplish a like change —

$$\begin{tikzcd}
2(\mathrm{C_6H_5})_3\mathrm{C} \arrow[dd] & + & \mathrm{I}_2 \arrow[d] & \rightarrow & 2(\mathrm{C_6H_5})_3\mathrm{CI} \\
 & & \overset{+}{\mathrm{I}}\text{---}\overset{-}{\mathrm{I}} \arrow[d] & & \\
2(\mathrm{C_6H_5})_3\overset{+}{\mathrm{C}} & + & (2\ominus + \overset{+}{\mathrm{I}} + \overset{-}{\mathrm{I}}) & \rightarrow & 2(\mathrm{C_6H_5})_3\overset{+}{\mathrm{C}}\text{---}\overset{-}{\mathrm{I}}
\end{tikzcd}$$

C. Addition of Hydrogen.

In the preceding reactions (1) and (2), the tervalent methyl carbon atom of triphenylmethyl functioned as a reducing agent by losing an electron, and thereby becoming quadrivalent through the development of a positive valence. On the other hand, when triphenylmethyl combines with hydrogen, the methyl carbon atom becomes quadrivalent through the acquisition of an electron, i.e., the development of a negative valence. In this respect, triphenylmethyl may be said to resemble certain non-metals.

Previously it has been noted that only negative hydrogen ($\overset{-}{\mathrm{H}}$) or neutral hydrogen (H) acts as a reducing agent. $\overset{-}{\mathrm{H}} \rightarrow \mathrm{H} + \ominus$, $\mathrm{H} \rightarrow \overset{+}{\mathrm{H}} + \ominus$. Positive hydrogen does not act as a reducing agent because the further loss of an electron would render hydrogen bivalent, an unknown condition. $\overset{+}{\mathrm{H}} \rightarrow \overset{++}{\mathrm{H}} + \ominus$. Hence, the interaction of the electrically neutral triphenylmethyl and neutral atomic hydrogen is perfectly analogous to the union of chlorine and hydrogen atoms —

$$\begin{tikzcd}
\mathrm{H} \arrow[d] & + & \mathrm{Cl} & \rightarrow & \mathrm{HCl} \\
\overset{+}{\mathrm{H}} & + \ominus + & \mathrm{Cl} & \rightarrow & \overset{+}{\mathrm{H}}\text{---}\overset{-}{\mathrm{Cl}}
\end{tikzcd}$$

Atomic hydrogen reduces atomic chlorine to negative chlorine, or, in equivalent terms, atomic chlorine oxidizes atomic hydrogen to positive hydrogen In the following scheme, atomic hydrogen reduces the tervalent methyl carbon atom, which, acquiring a negative valence, becomes quadrivalent in triphenylmethane —

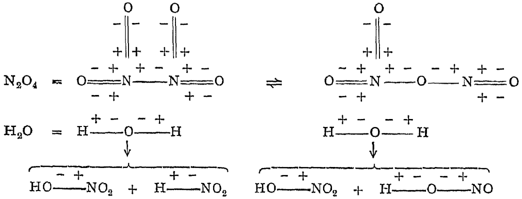
$$\begin{array}{l} H \quad + \quad (C_6H_5)_3C \rightarrow HC(C_6H_5)_3 \\ \downarrow \\ \overset{+}{H} + \ominus + (C_6H_5)_3C \rightarrow H\overset{+\quad-}{\text{——}}C\ (C_6H_5)_3 \end{array}$$

D. Reaction with Nitrogen Dioxide (or Tetroxide).

Schlenck and Mair[102] found that nitrogen dioxide on interaction with triphenylmethyl yielded simultaneously two products as indicated in the equation—

$$2(C_6H_5)_3C + 2NO_2\ (\text{or } N_2O_4) \rightarrow \underset{\substack{\text{(triphenyl-}\\\text{nitromethane)}}}{(C_6H_5)_3C\ NO_2} + \underset{\substack{\text{(triphenyl-}\\\text{methylnitrite).}}}{(C_6H_5)_3C\ ONO}$$

In the electronic interpretation of this interesting reaction, the former compound must be regarded as a derivative of nitric acid, $HO\overset{-\quad+}{\text{——}}NO_2$, the latter, a derivative of nitrous acid, $H\overset{+\quad-}{\text{——}}NO_2$, or $H\overset{+\quad-}{\text{——}}O\overset{-\quad+}{\text{——}}NO$ The key to the interpretation is found in the fact that nitrogen tetroxide is hydrolyzed by water yielding nitric and nitrous acids The following scheme takes into account the tautomeric formulæ of N_2O_4, to which correspond the tautomeric forms of nitrous acid —



$$\begin{array}{lll} N_2O_4 = O\overset{-\,+}{\underset{-\,+}{=\!=}}\overset{\overset{O}{\|}}{N}\overset{+\,-}{\text{——}}\overset{\overset{O}{\|}}{N}\overset{+\,-}{\underset{+\,-}{=\!=}}O & \rightleftharpoons & O\overset{-\,+}{\underset{-\,+}{=\!=}}\overset{\overset{O}{\|}}{N}\overset{+\,-}{\text{——}}O\overset{-\,+}{\text{——}}N\overset{+\,-}{\underset{+\,-}{=\!=}}O \\ H_2O = H\overset{+\,-}{\text{——}}O\overset{-\,+}{\text{——}}H & & H\overset{+\,-}{\text{——}}O\overset{-\,+}{\text{——}}H \\ \quad\downarrow & & \quad\downarrow \\ HO\overset{-\,+}{\text{——}}NO_2 + H\overset{+\,-}{\text{——}}NO_2 & & HO\overset{-\,+}{\text{——}}NO_2 + H\overset{+\,-}{\text{——}}O\overset{-\,+}{\text{——}}NO \end{array}$$

Each of the five valences of the nitrogen atom in nitric acid is positive, but in nitrous acid four are positive, and one is negative. Hence, in the tautomer H—O—N = O, nitrogen is tervalent since one positive and one negative valence are polarized Note also that one nitro-radical functions positively, while the other (either NO_2 or ONO) functions negatively Therefore, when one molecule of triphenylmethyl loses an electron and functions positively, another molecule of triphenylmethyl acquires that electron and functions negatively Consequent union of negative triphenylmethyl with the positive nitro-radical yields triphenylnitromethane, while union of positive triphenylmethyl with the negative nitro-radical yields triphenylmethylnitrite These changes are indicated as follows —

$$2(C_6H_5)_3C \rightarrow (C_6H_5)_3\overset{-}{C} + (C_6H_5)_3\overset{+}{C}$$

$$N_2O_4 = 2NO_2 \rightarrow \overset{+}{N}O_2 + \overset{-}{N}O_2 \text{ or } \overset{-}{O}NO$$

$$\swarrow \qquad\qquad \searrow$$

$$(C_6H_5)_3C\overset{-\;\;+}{\text{———}}NO_2 \quad (C_6H_5)_3C\overset{+\;\;-}{\text{———}}NO_2 \text{ or } (C_6H_5)_3C\overset{+\;\;-}{\text{———}}ONO$$

It should also be noted that, depending upon conditions, the dissociation of nitrogen tetroxide may proceed either ionically or molecularly In aqueous solution, the dissociation is presumably ionic, $N_2O_4 = (NO_2)\overset{+\;\;-}{\text{———}}(NO_2) \rightleftharpoons \overset{+}{N}O_2 + \overset{-}{N}O_2$, since hydrolysis yields nitric and nitrous acids as indicated above But when nitrogen tetroxide is heated to 140°, its density corresponds to the dioxide formula Is it not possible that NO_2, in which *nitrogen is quadrivalent,* exists as a free radical just as $(C_6H_5)_3C$ is a free radical in which *carbon is tervalent?* Or, is not the dissociation of associated triphenylmethyl (hexaphenylethane) exactly parallel to the dissociation of associated nitrogen dioxide (nitrogen tetroxide)? This is quite evident from the following equilibria —

$$(C_6H_5)_3C\ \ C(C_6H_5)_3 = (C_6H_5)_3C\overset{+\;\;-}{\text{———}}C(C_6H_5)_3 \rightleftharpoons (C_6H_5)_3C + (C_6H_5)_3C$$

$$N_2O_4 = (NO_2)\overset{+\;\;-}{\text{———}}(NO_2) \rightleftharpoons NO_2 + NO_2$$

In each of the above non-ionic dissociations, the positive radical becomes neutral, or is reduced to a free radical, through the acquisition of an electron from the negative radical which is thereby also rendered neutral, i e, it is oxidized to a free radical

These points of view may be summarized as follows In ionic dissociation $(A\overset{+\;\;-}{\text{——}}B \rightleftharpoons \overset{+}{A} + \overset{-}{B})$ the atoms or radicals maintain their respective charges In molecular dissociation $(A\overset{+\;\;-}{\text{——}}B \rightleftharpoons A + B)$ the atoms or radicals become electrically neutral through the transference of electrons from the negative radical to the positive radical Thus, free radicals are formed, and their activity is a factor of their further tendency either to gain or lose electrons. In electronic tautomerism[103]—

$$(\overset{+}{A}\text{—}\overset{-}{B} \rightleftharpoons A + B \rightleftharpoons \overset{-}{A}\text{—}\overset{+}{B})$$

a further transference of electrons reverses the polarity of the constituent atoms or radicals, and in this change *the intermediate, electrically neutral atoms or molecules (A and B) are essentially free radicals These points of view serve to emphasize the definition of a free radical as an electrically neutral atom or molecule which is capable of developing either positive or negative valences depending upon certain conditions which effect the loss or gain of electrons*

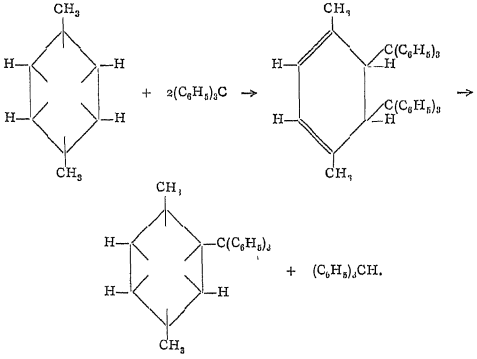
In the following interpretations of (E) the addition of xylene, (F) the action of acids, and (G) the action of light, the *electronic formula of benzene* plays an essential part

E. Addition of Xylene.

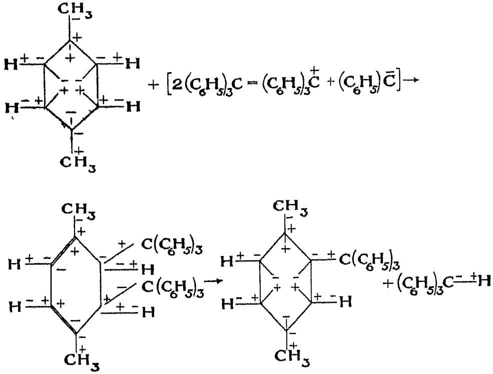
Wieland and Muller[104] found that the heating together of triphenylmethyl and xylene yielded dimethyltetraphenylmethane

$$2(C_6H_5)_3C + C_6H_4(CH_3)_2 = (C_6H_5)_3C\ C_6H_3\ (CH_3)_2 + (C_6H_5)_3CH$$

They interpreted the reaction as proceeding in two stages first, the union of two molecules of triphenylmethyl with one molecule of xylene, second, the elimination of one molecule of triphenylmethyl with a hydrogen atom of the benzene nucleus These reactions are indicated in the following scheme which employs centric formulæ —



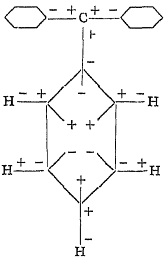
Every detail of this scheme may be correlated perfectly with the electronic formula of benzene, and with the previously described mechanism of substitution involving the centric valences of the benzene nucleus. It has been shown that, as a general rule, when hydrogen atoms or substituents in positions 1, 3, and 5 are negative, hydrogen atoms or substituents in positions 2, 4, and 6 are positive, and vice versâ. Furthermore, the polarity of a centric valence of a given carbon atom of the benzene nucleus was shown to be opposite in sign to the polarity of the hydrogen atom or substituent united to that carbon atom. Now the capacity of the methyl carbon atom of triphenylmethyl to develop either a positive or a negative valence has been demonstrated in preceding paragraphs. Accordingly, the addition of two molecules of triphenylmethyl to two of the centric valences of the nucleus, depends upon one molecule of triphenylmethyl functioning positively while the other molecule functions negatively. The electronic interpretation of the interaction of triphenylmethyl and xylene is embodied in the following scheme:—



$$+\ \left[2(C_6H_5)_3C = (C_6H_5)_3\overset{+}{C} + (C_6H_5)_3\overset{-}{C}\right] \rightarrow$$

From the above it is evident that the interaction of triphenylmethyl and xylene is not, strictly speaking, an addition reaction, but rather a substitution reaction conforming to, and thereby substantiating, not only the mechanism of substitution presented in previous chapters, but also the capacity of triphenylmethyl to function as a positive ion and as a negative ion.

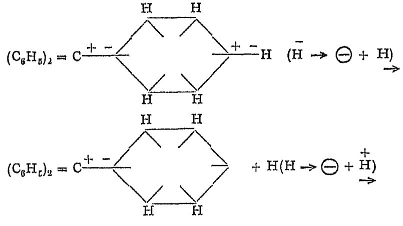
In considering (F) the action of acids, and (G) the action of light upon triphenylmethyl, the electronic formulæ of the benzene nuclei of triphenylmethyl are involved The phenyl radical is commonly spoken of as being negative in character, but if two phenyl radicals are united directly, as in diphenyl, the electronic conception of valence regards one phenyl as negative while the other is positive $(C_6H_5)\overset{+\ -}{\text{———}}(C_6H_5)$ Now triphenylmethane is generally made, either from benzal chloride, or from chloroform, through replacement of chlorine by phenyl Hydrolysis of either of these halogen compounds by potassium hydroxide effects the replacement of chlorine by negative hydroxyl From this standpoint, the chlorine atoms function negatively, and their replacement by phenyl radicals would indicate that the latter are also negative in triphenylmethane, and in triphenylmethyl Hence the electronic formula for triphenylmethyl, in which the valences of only one of the phenyl groups need be indicated, is as follows —



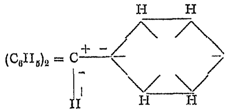
It should be observed that the hydrogen atoms in the ortho- and para-positions are negative The tendency for negative hydrogen to lose an electron and become neutral $(\overset{-}{H} \rightarrow \ominus + H)$ and the further tendency for neutral hydrogen to lose an electron, and become positive $(H \rightarrow \ominus + \overset{+}{H})$ has been considered previously in connection with various reactions and interpretations.

Therefore, it may naturally be assumed that the negative hydrogen atoms of the benzene nucleus are possibly less stable, in the above sense, than the positive hydrogen atoms Moreover, if we consider, for example, the negative para-hydrogen atom in the above formula of triphenylmethyl, what would be the immediate consequences of its becoming neutral through the loss of an electron? The positive valence of the para-carbon atom would be obliterated (neutralized or polarized) by the negative electron from the para-hydrogen atom In other words, the para-carbon atom would be reduced to the tervalent state, and the resulting neutral hydrogen atom would be free or dissociated But its further tendency to lose another electron and thereby become positive might naturally lead to its immediate attachment to the unsaturated trivalent methyl-carbon atom which would develop a negative valence through the acquisition of the electron from the neutral hydrogen atom, and thereby hold in combination the resulting positive hydrogen atom These changes (intramolecular rearrangements) are illustrated in the following scheme —

Formula I


H
H
$(C_6H_5)_2 = C$
+ −
+ −
H
$(\bar{H} \rightarrow \ominus + H)$
H
H
H
H
$(C_6H_5)_2 = C$
+ −
$+ H(H \rightarrow \ominus + \overset{+}{H})$
H
H

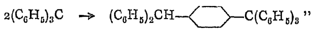
Formula II



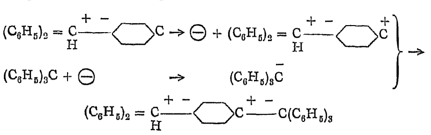
This scheme, based upon the tendency of negative hydrogen to function positively, affords both an explanation and a mechanism of the wandering of the para-hydrogen atom to the methyl carbon atom, and also shows how the para-carbon atom in formula I for triphenylmethyl is rendered tervalent in the tautomeric modification of formula II In other words, the methyl carbon atom of tautomer I is tervalent, the para-carbon atom of tautomer II. is tervalent The existence of tautomer II readily lends itself to, and is the essential feature of, the following interpretation (F) of the action of acids upon triphenylmethyl

F. Action of Acids.

Concerning the action of acids upon triphenylmethyl, Gomberg states that "Hydrochloric acid, and undoubtedly other acids, exert a peculiar catalytic influence upon triphenylmethyl The unsaturated, unstable hydrocarbon is thus converted in the presence of small quantities of acids, into an isomeric stable hydrocarbon. This hydrocarbon was first prepared by Ullmann and Borsum, directly from triphenylchloromethane, and later by the writer from triphenylmethyl as mentioned above It was first taken for the true stable hexaphenylethane But Tschitschibabin definitely proved its constitution to be that of *p*-benzylhydryltetraphenylmethane The rearrangement takes place thus —

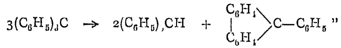


This reaction is readily interpreted by the existence of tautomer II (see preceding scheme) in which the para-carbon atom of one of the phenyl radicals is in the tervalent state The union of this carbon atom of tautomer II with the tervalent methyl carbon atom of tautomer I would naturally take place because the para-carbon atom originally possessed a positive valence, and, therefore, tends to lose an electron, and thus again develop a positive valence In turn, this electron would be taken up by the unstable tervalent methyl-carbon atom of tautomer I Combination of the resulting oppositely charged tautomers would then yield parabenzhydryltetraphenylmethane according to the following scheme :—



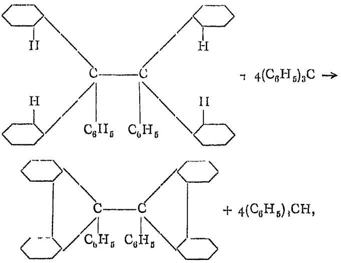
G. Action of Light.

Concerning the action of light, Gomberg has stated that "Solutions of triphenylmethyl in benzene are quite susceptible to light, especially direct sunlight. Like most photochemical processes of this type, the reaction in this instance also is auto-oxidation and reduction. Schmidlin showed that the following reaction takes place:—



$$3(C_6H_5)_3C \rightarrow 2(C_6H_5)_3CH + \begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}{>}C-C_6H_5 \text{"}$$

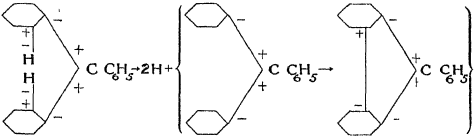
Schmidlin,[105] employing bi-molecular formulæ, has presented the following scheme for this reaction:—



and he states that "das leicht dissoziierbare Hexaphenyl-athan wird durch das Triphenylmethyl zum schwer dissoziierbaren, energiearmen Di-biphenylendiphenylathan reduziert."

Now the electronic formula for triphenylmethyl readily lends itself to an interpretation of this hitherto unexplained reaction. First, it should be observed that not only the hydrogen atoms in the para-positions to the attachment of the methyl carbon atom, but also the ortho-hydrogen atoms, are negative. On the other hand, the methyl hydrogen atom of triphenylmethane (one of the reaction products) is positive. Therefore, the auto-oxidation and reduction effected by light involves the transition of negative hydrogen atoms from the ortho-positions to the unsaturated methyl carbon atom of triphenylmethane. Here again the relatively unstable negative ortho-hydrogen atoms first become neutral, $\overset{-}{H} \rightarrow H + \ominus$, and the negative electron obliterates the positive valence of the ortho-carbon atom thus making it tervalent. The neutral or free hydrogen atom becomes positive through the loss of an electron, $H \rightarrow \overset{+}{H} + \ominus$, which renders the unsaturated methyl carbon atom of triphenylmethyl negative. Union of negative triphenylmethyl with positive hydrogen then yields triphenylmethane, and the union of the ortho-tervalent carbon atoms, by the transfer of an electron from one to the other, completes the formation of biphenylenediphenylethane. Employing the briefer unimolecular formulæ, the electronic interpretation is embodied in the following schemes (1) and (2). The first shows the effect of the conversion of the ortho-negative hydrogen atoms to the free or neutral state, and the union of the resultant ortho-tervalent carbon atoms, which reaction is an *intramolecular oxidation and reduction*. The second shows the reducing action of the neutral hydrogen upon triphenylmethyl yielding triphenylmethane.

(1)



(2)

$$\left.\begin{array}{l} 2H \quad \rightarrow 2\ominus + 2\overset{+}{H} \\ 2(C_6H_5)_3C + 2\ominus \rightarrow 2(C_6H_5)_3\overset{-}{C} \end{array}\right\} \rightarrow 2(C_6H_5)_3C\overset{-\;+}{—}H$$

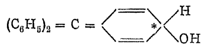
Thus the action of light in this particular instance involves the change, $\overset{-}{H} \rightarrow \overset{+}{H} + 2\ominus$. In this connection it may be of interest to recall that in the preceding chapter the action of light in effecting nucleus substitution in the side-chain was shown to involve the conversion of positive halogen to negative halogen, $\overset{+}{Cl} \rightarrow \overset{-}{Cl} + 2\oplus$. These processes are analogous in that each involves auto-oxidation and reduction.

H. Electrical Conductivity.

Gomberg found that the triarylmethylhalides behaved truly like salts in that they manifest molecular conductivities which increase with the dilution He states "It was thus definitely established that there are 'carbonium' salts in the true sense of the definition applied to salts The conclusion was drawn that the basic properties, by virtue of which the salt formation occurs, reside in the central methyl carbon atom" This conclusion is still held by some, but Gomberg later gave up this interpretation, presenting evidence which favoured the *quinol hypothesis* Accordingly, he states that "since the manifestation of colour and the salt-like properties of these substances are simultaneous, the conclusion seems warranted that both these phenomena are the results of one and the same cause, i e, tautomerization to the quinoid state Consequently, these salts were named *quinocarbonium salts* corresponding to the *quinocarbonium base* —

$(C_6H_5)_3C\ \ OH$

(Carbinol, *pseudo-base*)

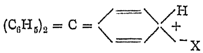


(Quinocarbonium base)

"For obvious reasons, the basicity was now assumed to lie in the quinone nucleus, in the C* and not in the central carbon atom as had been originally supposed"

From these two points of view, triphenylmethylchloride (or other halides) may be represented electronically as carbonium or quinocarbonium salts by the respective formulæ—

$(C_6H_5)_3\overset{+}{C}\overset{-}{\text{——}}X$

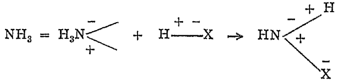


Since hydrolysis with potassium hydroxide yields potassium halide and the base, it follows that the triphenylmethyl ion (either formula) is positive This brings us to consider the "unexpected discovery that triphenylmethyl itself behaves like an electrolyte when dissolved in liquid sulphur dioxide,"[106] and concerning which Gomberg has raised the question in these words · "How is this strange phenomenon, a hydrocarbon behaving like an electrolyte, to be accounted for? Several explanations have been offered, but none of these is entirely satisfactory"

Now since triphenylmethyl has been shown to act similarly to metallic sodium in several reactions (notably Section A and B of this chapter) for which the electronic interpretations were based upon the parallel tendencies—$Na \rightarrow \overset{+}{Na} + \ominus$, and

$(C_6H_5)_3C \rightarrow (C_6H_5)_3\overset{+}{C} + \ominus$—*is it not possible that the electrical conductivities of sodium in liquid ammonia, and triphenylmethyl in liquid sulphur dioxide, are perfectly analogous phenomena interpretable in similar terms?*

An explanation of the conductivity of sodium in liquid ammonia solution will be considered first. Cady,[107] and later Franklin and Kraus,[108] found that when sodium was dissolved in liquid ammonia, the solution was a good conductor, *but there was no visible separation of any products of electrolysis at the electrodes, neither were there any signs of polarization*. Since conductivity presupposes the existence of positive and negative ions, perhaps the simplest explanation of the formation of ions in this case depends upon the change, $Na \rightarrow \overset{+}{Na} + \ominus$, which at once accounts for the positive ions. But what disposition is to be made of the negative electron? What is its function? The nitrogen atom in ammonia is tervalent but is regarded as unsaturated since it possesses potentially one free positive and one free negative valence as evidenced by its combination with water $(\overset{+}{H}\ \overset{-}{OH})$ or hydrogen halide $(\overset{+}{H}\ \overset{-}{X})$ —



Hence, it may be assumed that the negative electron (from sodium) neutralizes or polarizes the potential positive valence of the nitrogen atom of ammonia thereby developing a negative valence —

$$Na \rightarrow \overset{+}{Na} + \ominus,$$

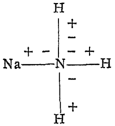
$$NH_3(= H_3N\pm) + \ominus \rightarrow \overset{-}{NH_3}$$

In other words, the ammonia molecule is converted into a negative ammonia ion. With positive sodium ions and negative ammonia ions, conductivity is readily explained. Sodium ions are discharged at the cathode $(\overset{+}{Na} + \ominus \rightarrow Na)$ and the liberated metallic sodium immediately dissolves and reionizes in the liquid ammonia. The negative ammonia ions are simultaneously discharged at the anode with the immediate regeneration of molecular ammonia ($\overset{-}{NH_3} + \oplus \rightarrow NH_3$). This scheme not only accounts for (1) the conductivity, but also explains (2) the absence of products of electrolysis at the electrodes, and (3) non-polarization

Other facts will now be considered which substantiate the preceding explanation One of the difficulties encountered in conductivity measurements on solutions of sodium in liquid ammonia is the marked decrease in concentration of sodium through interaction of solute and solvent forming sodamide and hydrogen —

$$2Na + 2NH_3 \rightarrow 2Na\ NH_2 + H_2$$

What is the mechanism of this reaction? The existence of the ions, $\overset{+}{Na}$ and $\overset{-}{NH_3}$, affords a logical interpretation Corresponding to the ions in a given solution, there is always the possibility of the existence of some undissociated molecules. In this instance, union of the ions, $\overset{+}{Na}$ and $\overset{-}{NH_3}$, would yield the molecule, sodium ammonia, Na NH_3, the complete electronic formula being—

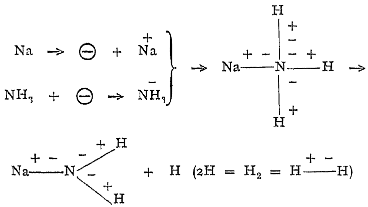


It is at once evident that this compound is exceptional in that its nitrogen atom is quadrivalent Let it now be recalled that just as carbon is tervalent in $(C_6H_5)_3C$, so nitrogen was shown to be quadrivalent in NO_2, and each of these compounds may be regarded as a free radical Their reactivity was explained by the abnormal valence of the carbon and nitrogen atoms and their tendencies to revert to the normal valence by gain or loss of electrons In the same sense, the above sodium-ammonia compound may be regarded as a free radical—an unstable compound containing quadrivalent nitrogen * Greater

---

* This conception of a *free radical* embraces the interesting and significant organic amalgams prepared by McCoy and Moore [109] For example, tetramethyl ammonium amalgam was prepared by the electrolysis of cold alcoholic solutions of tramethyl ammonium chloride using a mercury cathode. In this reaction, the

stability would ensue if the nitrogen atom became tervalent through the loss of an electron, and, if one of the $\overset{+}{H}$ atoms acquires this electron, that hydrogen atom would be rendered neutral, i e, free or dissociated, and sodium amide would be formed. Combination of liberated hydrogen atoms yields molecular hydrogen The complete electronic scheme for the formation of sodium and ammonia ions, molecular sodium ammonia, and sodium amide and hydrogen, is as follows —



tetramethyl ammonium ion (in which nitrogen is quinquevalent) loses its positive charge or valence whereupon the nitrogen atom is rendered *quadrivalent*,

$$(CH_3)_4\overset{+}{N} + \ominus \rightarrow (CH_3)_4N$$

(dissolved in Hg) In other words, tetramethyl ammonium, $(CH_3)_4N$, is a free radical in the same sense that NO_2 and $NaNH_3$ are free radicals *Each is a compound of quadrivalent nitrogen* The instability or reactivity of tetramethyl ammonium is due to the tendency of its nitrogen atom to develop a positive valence through the loss of an electron This explains its vigorous reaction with water yielding tetramethyl ammonium hydroxide and hydrogen —

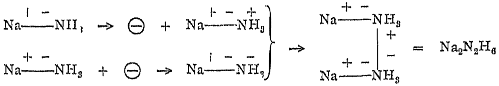
$$\begin{array}{ccccc} (CH_3)_4N & \rightarrow & (CH_3)_4\overset{+}{N} & + & \ominus \\ H\ OH & \rightarrow & \overset{-}{OH} & + & \overset{+}{H} \\ & & \downarrow & & \downarrow \\ & & (CH_3)_4\overset{+}{N}\ \overset{-}{OH} & & H\ (2H = H_2 = \overset{+}{H}—\overset{-}{H}) \end{array}$$

McCoy and Moore state that the tetramethyl ammonium radical acts on solutions of copper and zinc salts, replacing these metals in the salts and setting free the metals themselves. The electronic scheme is as follows —

$$2(CH_3)_4N \rightarrow 2(CH_3)_4\overset{+}{N} + 2\ominus,$$
$$\overset{++}{Cu} + 2\ominus \rightarrow Cu$$

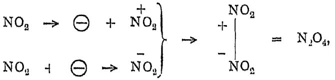
These reactions show the striking analogy existing between free radicals and metals, their behaviour being identical in many instances

Further evidence for the existence of the sodium-ammonia compound formed by the union of the ions $\overset{+}{Na}$ and $\overset{-}{NH_3}$ is afforded by the work of Joannis[110] showing that in solutions of sodium in liquid ammonia, two molecules of sodium unite with two molecules of ammonia forming $Na_2N_2H_6$. This is readily explained by the existence of the free radical, $Na\,.\,NH_3$, in which nitrogen is quadrivalent The tendency for two such free radicals to associate would lead to the formation of $Na_2N_2H_6$ according to the following scheme —



$$\left.\begin{array}{l} Na\overset{|\ -}{\text{——}}NH_3 \rightarrow \ominus + Na\overset{+\ -\ +}{\text{——}}NH_3 \\ Na\overset{+\ -}{\text{——}}NH_3 + \ominus \rightarrow Na\overset{|\ -\ -}{\text{——}}NH_3 \end{array}\right\} \rightarrow \begin{array}{l} Na\overset{+\ -}{\text{——}}NH_3 \\ \qquad\quad {}^{+}_{-}| \\ Na\overset{+\ -}{\text{——}}NH_3 \end{array} = Na_2N_2H_6$$

The above reaction is exactly parallel to the union of the two free radicals, nitrogen dioxide, to form nitrogen tetroxide—

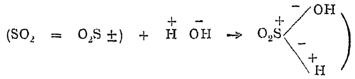


$$\left.\begin{array}{l} NO_2 \rightarrow \ominus + \overset{+}{NO_2} \\ NO_2 + \ominus \rightarrow \overset{-}{NO_2} \end{array}\right\} \rightarrow \begin{array}{c} NO_2 \\ {}^{+}_{-}| \\ NO_2 \end{array} = N_2O_4,$$

or to the union of two free radicals of triphenylmethyl to form hexaphenylethane as previously described.

Having shown that the conductivity of solutions of sodium in liquid ammonia may be explained by the existence of the ions, $\overset{+}{Na}$ and $\overset{-}{NH_3}$, and that their union yields the free radical $Na\,.\,NH_3$, the instability of this radical in turn explained the formation of $NaNH_2$ and of $Na_2N_2H_6$ The quadrivalent nitrogen atom in $Na\,.\,NH_3$ became tervalent in forming $NaNH_2$, and quinquevalent in the compound $Na_2N_2H_6$ The conductivity of solutions of triphenylmethyl in liquid sulphur dioxide may now be considered.

The triphenylmethyl molecule is converted into a positive ion by the loss of an electron (either from the methyl carbon atom or from the para-carbon atom of the quinone ring, quino-carbonium base). This electron converts a sulphur dioxide molecule into a negative ion. This follows from the fact that sulphur dioxide, like ammonia, possesses potentially one free positive and one free negative valence (Combination with water yields a tautomeric form of sulphurous acid, thus—



$$(SO_2 = O_2S\pm) + \overset{+}{H}\ \overset{-}{OH} \rightarrow O_2\overset{+}{S}\begin{matrix}\overset{-}{}OH \\ \overset{-}{} \\ \overset{+}{}H\end{matrix}\Bigg)$$

The negative electron from triphenylmethyl polarizes the potential positive valence of the sulphur atom of sulphur dioxide thereby developing a free negative valence In other words, the triphenylmethyl molecule becomes a positive ion and the sulphur dioxide molecule becomes a negative ion according to the scheme of the following reactions (1) and (2) —

$$(1)\ (C_6H_5)_3C \rightarrow \ominus + (C_6H_5)_3\overset{+}{C}$$

$$(2)\ O_2S\pm + \ominus \rightarrow \overset{-}{SO_2}$$

The existence of these ions would account for the conductivity of triphenylmethyl in liquid sulphur dioxide solution. The products of electrolysis are triphenylmethyl at the cathode through the reversal of reaction (1), and sulphur dioxide at the anode through the reversal of reaction (2), or the equivalent change, $\overset{-}{SO_2} + \oplus \rightarrow SO_2$. This scheme is identical in principle with the scheme for the ionization of sodium and ammonia previously described

Summary

Briefly summarized, the interpretations of a number of the characteristic properties of free radicals, particularly triphenylmethyl, in terms of the electronic conception of positive and negative valences, have led to the following conclusions .—

(1) Free radicals are comparable in many respects to the *electrically neutral atomic state.*

(2) The instability, or reactivity, and general chemical properties of free radicals depend upon their development of positive or negative valences through the loss or gain, respectively, of negative electrons In other words, free radicals may act either as reducing or as oxidizing agents

(3) The adaptibility and tendency to lose or to gain electrons are properties of certain atoms in the free radicals The valences of these atoms are variable both as to number and to polarity

(4) Not only triphenylmethyl and other triarylmethyls, but

also nitrogen dioxide, sodium-ammonium, tetramethyl ammonium, and other compounds, as well as certain elements, may be regarded as free radicals

(5) Some of the peculiar rearrangement reactions manifested by triphenylmethyl are readily interpreted by means of the *electronic formula of benzene*

(6) Evidence is presented in support of the view that there is a close analogy between the electrical conductivity of triphenylmethyl in liquid sulphur dioxide solution, and the conductivity of sodium dissolved in liquid ammonia. In the former instance, the ions are $(C_6H_5)_3\overset{+}{C}$ and $\overset{-}{SO_2}$, in the latter, $\overset{+}{Na}$ and $\overset{-}{NH_3}$ The existence of these ions is substantiated by the formation in solution of the free radical, sodium-ammonium, $NaNH_3$, the electronic formula of which lends itself to an interpretation of, and a mechanism for, the reaction in which sodium amide is formed, as well as the compound $Na_2N_2H_6$.

(7) Finally, it is hoped that the definition and conception of *free radicals* (herewith developed, applied, and confirmed by interpretations of numerous reactions) may prove to be free from the more or less vague and mystical ideas which have characterized the use of the term "free radical" in the history of chemistry.

It is only through the employment of the electronic conception of positive and negative valences and electronic formulæ that the interpretations of the existence and properties of free radicals, and the general conclusions here presented, are possible. The literature upon this subject shows that ordinary structural formulæ afford very limited aid

PART III.

PHYSICAL PROPERTIES AND PHYSICO-CHEMICAL PHENOMENA MOLECULAR VOLUMES, ABSORPTION OF LIGHT AND FLUORESCENCE

CHAPTER XVII.

THE ELECTRONIC FORMULÆ AND MOLECULAR VOLUMES OF THE CHLOROBENZENES

IN Part II., Chapters VII to XVI inclusive, the constitution of benzene, substitution in the benzene nucleus, and the chemical properties of benzene, as well as many of its derivatives, have been interpreted in terms of the electronic conception of valence and the electronic formula of benzene. The purpose of Part II. has been to substantiate the electronic conception of valence and the electronic formula of benzene chiefly by the enumeration, explanation, and interpretation of *chemical properties and reactions*. There now remain many *physical properties* and *physico-chemical phenomena*, such as molecular volume data, light absorption, and fluorescence data to be explained in terms of the electronic conception of positive and negative valence. The discussion and proposed interpretation of these physical and physico-chemical phenomena constitute the subject matter of Part III., Chapters XVII. to XXII. inclusive

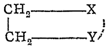
A. Molecular Volume Anomalies.

Further evidence for the electronic formula of benzene may be found in the development of a relationship between the electronic formulæ and the molecular volumes of mono-, di-, tri-, tetra-, penta-, and hexa-chlorobenzenes. What are the essential features of the relationship existing between the molecular volumes of these six compounds and their respective electronic formulæ?

Apropos of this question, consider the remarkable anomaly first noted by Staedel[111] that β-halogen compounds always possess smaller molecular volumes than their isomeric α-halogen compounds. For instance, the molecular volume of CH_3CHXCH_2X is about three units less than that of $CH_3CH_2CHX_2$. Thus, two structurally similar molecules may possess different molecular volumes, and there is nothing in the ordinary structural formulæ of these isomers to account for, or to correlate, these differences

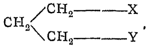
Le Bas[112] has proposed an explanation of some of these anomalies in his hypothesis of partial or incomplete rings, and his examination of the molecular volumes of numerous compounds has led to the following results[113] which must be considered in this paper (*a*) If a paraffin compound be substituted by a halogen atom or other unsaturated substituent more than once, the volume of the compound is normal, or subject to the additive rule, provided that the substituents be attached to a single carbon atom (*b*) If they are distributed among several carbon atoms, there are always contractions of a constituent nature It matters not how many hydrogen atoms of the terminal carbon are substituted, the contractions are dependent upon the number substituted in the β-position (*c*) For one substitution in the β-position the contraction is a little over three units For two substitutions in the β-position the contraction is about six units, or nearly double the first Substitutions in the γ-position always involve greater contractions than substitutions in the β-position, and it is conceivable that substituents in the δ-position would result in still greater contractions

In explanation of these results Le Bas[114] states that intermediate between open and closed chain compounds are what are known as partial or incomplete rings "In order that they may be formed, it is necessary that two atoms or groups, which may be supposed to possess residual affinity, occur in a hydrocarbon chain attached to different carbon atoms If the carbons are near to each other, there is no need to suppose any variation from structure usually considered when the tetrahedral arrangement of the valency links of carbon is understood The additional feature of curvature of the hydrocarbon chain may also be the normal condition of things In the case of saturated compounds the plane formulæ are figured thus —



$$\begin{array}{l} CH_2 — X \\ | \qquad\quad\ \ \vdots \\ CH_2 — Y \end{array}$$

If the two attracting groups are united to carbons not in the immediate neighbourhood of each other, we must suppose that they are brought near by the curvature of the hydrocarbon chain, or the alternative supposition just given is true In any such case, such a structure affects the molecular volumes of compounds" Thus —

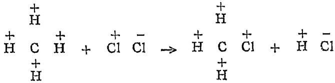


It is not the purpose of this chapter to disparage or discredit the explanation of Le Bas, but, rather, to propose a new explanation based upon the electronic conception of positive and negative valences as follows Halogen atoms (and other substituents) may function positively or negatively Halogen atoms substituted in the α-position alone, or in the β-position alone, cause no contraction, but each of the halogen atoms in the β-position occasions a contraction of about three units provided one or more halogen atoms are present in the α-position May we not assume, then, that *the differences or contractions in the molecular volumes of the isomers are due to differences in the polarities of the halogen atoms or substituents, in the* α- *and* β-*positions respectively?* Further, may we not assume that *differences in polarity are directly related to differences in the relative atomic volumes of the halogen atoms or substituents?* For purposes of illustration, suppose that the halogen atoms in the α-position function positively, while those in the β-position function negatively (evidence will be presented shortly) and that the atomic volume of $\overset{+}{X}$ is greater than that of $\overset{-}{X}$ Then, electronic formulæ, such as $CH_3CH_2CH\overset{+}{X}\overset{+}{X}$, and $CH_3CH\overset{-}{X}CH_2\overset{+}{X}$, correlate the fact that the molecular volume of the α-di-substituted compound is greater than that of the isomeric α, β-di-substituted compound, the difference in the molecular volumes being due to differences in the atomic volumes of $\overset{+}{X}$ and $\overset{-}{X}$ * Such a correlation cannot be shown by employing the ordinary structural formulæ of the compounds in question

The above assumptions may now be correlated with a number of facts which are readily interpreted in terms of the electronic conception of positive and negative valences. It has been noted that when a paraffin compound undergoes substitution more than once, the molecular volumes of the substitution products are normal, i.e., subject to the additive rule, provided that the substituents are linked to a single carbon atom. In this connection consider the direct substitution of chlorine in methane which may be represented thus —

---

* It should be noted that when different atoms, such as chlorine and carbon, are united, a change in the polarity of one, involving a change in the polarity of the other, would concomitantly alter the atomic volumes of both atoms, but the atomic volume of each atom would not be altered to the same extent Accordingly, the molecular volume data under consideration in this chapter are regarded as a measure of certain additive and constitutive effects involving the polarity and the atomic volume of certain atoms.



$$\begin{array}{ccc} & \overset{+}{H} & \\ \overset{+}{H} & C & \overset{+}{H} \\ & \overset{+}{H} & \end{array} + \overset{+}{Cl}\;\overset{-}{Cl} \rightarrow \begin{array}{ccc} & \overset{+}{H} & \\ \overset{+}{H} & C & \overset{+}{Cl} \\ & \overset{+}{H} & \end{array} + \overset{+}{H}\;\overset{-}{Cl}$$

Successive substitution of positive chlorine atoms would result in the formation of compounds of formulæ,

$$C\overset{+}{H}_2(\overset{+}{Cl})_2,\ C\overset{+}{H}(\overset{+}{Cl})_3 \text{ and } C(\overset{+}{Cl})_4$$

If we tabulate the molecular volumes (V_m) of these compounds and the volumes of their hydrocarbon groups, the differences between these values will give the volumes of their chlorine atoms which are indicated under (nCl) in the following table, n being the number of chlorine atoms in the respective compounds —

Compound	(V_m)	Volume of Hydrocarbon Group	(nCl)
CH_2Cl_2	65.1	22.1	2 × 21.5
$CHCl_3$	84.5	18.5	3 × 22.0
CCl_4	103.7	14.8	4 × 22.2

The data show a slight increase in the atomic volumes of the chlorine atoms as they accumulate in the molecule. The electronic schemes for the substitution reactions (in the absence of intramolecular oxidation-reduction reactions) indicate that the substituted chlorine atoms function positively. The molecular volume data indicate that the average atomic volume of these positive chlorine atoms is very nearly equal to 22.0.

The next question to be considered naturally relates to the atomic volume of the chlorine atoms which function negatively. An extension of the hypothesis to the constitution and molecular volumes of ethylene and ethylidene dichlorides leads to some interesting conclusions. The values with respect to these isomers are as follows —

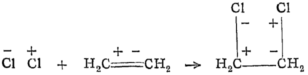
Compound	(V_m)	Volume of Hydro carbon Group	$(n\mathrm{Cl})$
$CH_3\ CHCl_2$	88·9	44·5	2 × 22·2
$CH_2Cl\ CH_2Cl$	85·3	44·5	2 × 20·4

From the data it appears that the average atomic volume of the chlorine atom in ethylidene dichloride is 22·2, in ethylene dichloride, 20·4. Correctly to interpret this constitutive effect, account must be taken of the fact that in the majority of the aliphatic compounds of the type RCl in which only one chlorine atom is substituted on a carbon atom, the average atomic volume of this single chlorine atom is 21·5. Since the chlorine atoms in ethylene dichloride are singly attached to separate carbon atoms and their total volume is 40·8, the volume of each cannot be 21·5. Consequently, it follows that if one of these chlorine atoms has the usual volume of 21·5, then the volume of the other chlorine atom must be 19·3, i.e., the difference between their total volumes, 40·8 and 21·5. While none of these values is absolute, the data indicate a possible correlation of molecular volume data and electronic formulæ. Thus, if the *α*-chlorine atom has a greater atomic volume than the *β*-chlorine atom and functions positively, then, in contra-distinction, the *β*-chlorine atom would be assumed to function negatively. The correlation of the electronic formulæ and atomic volumes of the chlorine atoms of ethylidene and ethylene dichlorides may be summarized thus.—

Isomers	$(n\mathrm{Cl})$	
$CH_3\ CH\overset{+}{Cl}\overset{+}{Cl}$	44·4	$(2\overset{+}{Cl} = 2 \times 22·2 = 44·4)$
$CH_2\overset{-}{Cl}\ CH_2\overset{+}{Cl}$	40·8	$(\overset{-}{Cl} + \overset{+}{Cl} = 19·3 + 21·5 = 40·8)$

From this point of view, the difference between the molecular volumes of ethylidene and ethylene di-chlorides is not dependent on the idea of the formation of a partial ring, as assumed by Le Bas in the case of ethylene dichloride, but is due to a difference in the atomic volumes of the *α*- and *β*-chlorine atoms which are assumed to function positively and negatively, respectively. Further evidence for the assumption of this difference of polarity is found in the union of chlorine with ethylene. The hydrolysis of chlorine (previously indicated) yielding hydrogen chloride

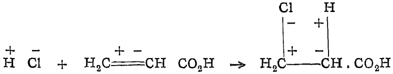
$(\overset{+}{H}\ \overset{-}{Cl})$ and hypochlorous acid $(\overset{-}{HO}\ \overset{+}{Cl})$ indicates that the chlorine molecule may yield $\overset{+}{Cl}$ and $\overset{-}{Cl}$ on dissociation Accordingly, the addition of chlorine to ethylene is represented thus —



$$\overset{-}{Cl}\ \overset{+}{Cl} + H_2\overset{+}{C}{=\!=}\overset{-}{C}H_2 \rightarrow H_2\overset{\overset{Cl}{|-}}{\overset{+}{C}}-\overset{\overset{Cl}{+|}}{\overset{-}{C}}H_2$$

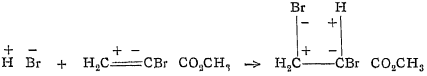
The "opening" of the double bond of ethylene may be regarded as the simultaneous development of a free positive valence on the one carbon atom and a free negative valence on the other, which valences, respectively, bind the negative and positive chlorine atoms In other words, the chlorine atoms in the α- and β-positions are of opposite polarity

An analogous situation, indicating that the α-substituent tends to function positively while the β-substituent is negative, is found in the addition of hydrogen chloride $(\overset{+}{H}\ \overset{-}{Cl})$ to acrylic acid yielding β-chloropropionic acid exclusively,* thus —



$$\overset{+}{H}\ \overset{-}{Cl} + H_2\overset{+}{C}{=\!=}\overset{-}{C}H\ CO_2H \rightarrow H_2\overset{\overset{Cl}{|-}}{\overset{+}{C}}-\overset{\overset{H}{+|}}{\overset{-}{C}}H.CO_2H$$

Note also in this connection the addition of hydrogen bromide to α-bromo acrylic ester Again the positive substituent unites with the α-carbon atom while the negative substituent assumes the β-position, thus —



$$\overset{+}{H}\ \overset{-}{Br} + H_2\overset{+}{C}{=\!=}\overset{-}{C}Br\ CO_2CH_3 \rightarrow H_2\overset{\overset{Br}{|-}}{\overset{+}{C}}-\overset{\overset{H}{+|}}{\overset{-}{C}}Br\ CO_2CH_3$$

This compound, α, β-di-bromopropionic ester, is also the product of the addition of bromine $(\overset{+}{Br}\ \overset{-}{Br})$ to acrylic ester, and in view of the preceding facts the α- and β-bromine atoms are, respectively, positive and negative. Now the molecular volume of α, β-di-bromopropionic ester is 3.9 units less than that of its isomer, the α, α-compound. Thus it appears that the α-substituents have a greater atomic volume than the β-substituents and a relationship exists between the electronic formulæ of these isomers and their molecular volumes which is summarized as follows:—

---

* Addition reactions involving the two types of double bonds, *diplex* $(\overset{+\ -}{\underset{+\ -}{C{=\!=}C}})$, and *contraplex* $(\overset{-\ +}{\underset{+\ -}{C{=\!=}C}})$ (Fry, *Z physik Chem*, 76, 400 (1911)), renders possible an interpretation of many of the anomalous addition reactions studied by Michael from the standpoint of his "chemical neutralization" theory.

$$(\alpha, \alpha)\ \mathrm{CH_3\ C\overset{+}{Br}\overset{+}{Br}\ CO_2CH_3}. \qquad V_m = 156.3$$

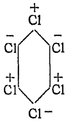
$$(\alpha, \beta)\ \mathrm{CH_2\overset{-}{Br}\ CH_2\overset{+}{Br}\ CO_2CH_3} \qquad V_m = \underline{152.4}$$

$$\text{Difference } (V\ \overset{+}{\mathrm{Br}} - V\ \overset{-}{\mathrm{Br}}) \qquad = 3.9$$

The preceding facts and their correlation with the electronic formulæ lead to the assumption that the atomic volume of the positive halogen substituent is greater than that of the negative halogen substituent. Consequently, the differences between the molecular volumes of the isomers in question is related in some way (to be considered later) to differences in the polarities of the substituents in the α- and β-positions. This hypothesis may now be extended to the explanation of the remarkable anomalies met with in the atomic volumes of the chlorine atoms in the several chlorobenzenes, especially hexa-chlorobenzene. The existence of a relationship between the molecular volumes of the chlorobenzenes and the electronic formula of benzene will be definitely indicated.

B. The Electronic Formulæ of the Chlorobenzenes

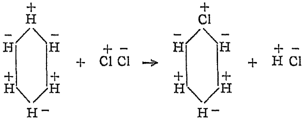
In previous chapters numerous facts have been presented and interpreted by means of the electronic formula of benzene. A substitution rule has been developed showing that when substituents are of the same sign or polarity they will occupy positions which are meta to each other, but if two substituents are of opposite sign or polarity they will occupy either ortho or para positions to each other. The development of this rule depended upon the fact that the electronic formula of benzene is the only formula which presents conjointly a structural basis and an electronic interpretation of the relations between ortho and para positions and substituents in contradistinction to meta positions and substituents. Now, if the electronic formula of benzene is subject to correlation with the molecular volumes of the chlorobenzenes, the following conditions must be fulfilled (1) Substituted chlorine atoms occupying ortho or para positions to each other must be of opposite polarity while those occupying meta positions to each other must be of the same polarity (2) It has been indicated that chlorine atoms which function positively possess a greater atomic volume than those which function negatively Consequently, positive chlorine atoms in the benzene nucleus must possess greater atomic volumes than the negative chlorine atoms in the corresponding para or ortho positions These conditions would be fulfilled completely if it is shown that, for instance, in hexa-chlorobenzene



the positive chlorine atoms in positions 1, 3, and 5 possess greater atomic volumes than the negative chlorine atoms in positions 2, 4, and 6 To this end, consider, first, the electronic schemes for the formation of the six chlorobenzenes whose molecular volumes present the remarkable anomalies that demand an explanation.

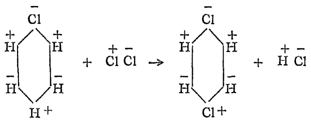
The direct substitution of chlorine in the benzene nucleus, generally effected with the aid of halogen carriers, corresponds to the following simplified scheme I —

Scheme I



in which positive chlorine is introduced The extended substitution of chlorine yields the several di-, tri-, tetra-, penta-, and hexa-chlorobenzenes Direct substitution, as indicated, effects the introduction of a positive substituent, but the electronic formula of benzene requires that poly-substituted derivatives embody negative substituents as well The existence of the negative substituents depends upon the electronic tautomerism (for example, $\overset{-}{C_6H_5}\overset{+}{Cl} \rightleftharpoons \overset{+}{C_6H_5}\overset{-}{Cl}$) of some of the derivatives which in turn undergo further substitution With reference to the formation of para-di-chlorobenzene, or any other di-substituted derivative, recall that if a given substituent in the benzene nucleus is positive, the entering positive substituent will occupy the meta position, but if the mono-substituent is negative, the entering positive substituent will occupy para or ortho positions The chlorination of mono-chlorobenzene yields chiefly para-di-chlorobenzene Consequently, electromer $\overset{+}{C_6H_5}\overset{-}{Cl}$ (and not electromer $\overset{-}{C_6H_5}\overset{+}{Cl}$) undergoes substitution according to scheme II —

Scheme II



Schemes I and II. in conjunction with the principle of electronic tautomerism show that a given positive substituent may, under certain conditions, function as a negative substituent, but in para-di-chlorobenzene the halogen atoms are of opposite polarity This not only follows from the electronic formulæ but is confirmed by experimental facts, notably the reactivity of the negative chlorine atom and the non-reactivity of the positive chlorine atom when para-di-chlorobenzene is heated with methyl alcohol solution of sodium methylate. *The reaction conforms quantitatively to the electronic equation* —

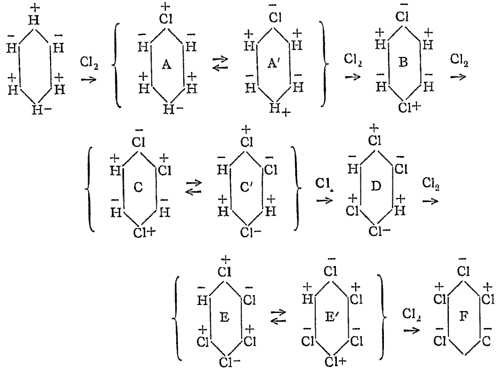
$$\overset{+}{Cl} \,.\, C_6H_4 \,.\, \overset{-}{Cl} + \overset{+}{Na} \,.\, OCH_3 \rightarrow \overset{+}{Cl} \,.\, C_6H_4 \,.\, \overset{-}{OCH_3} + \overset{+}{Na} \,.\, \overset{-}{Cl}$$

Another remarkable difference between the chlorine atoms in para-di-chlorobenzene will shortly be considered in connection with their atomic volumes

In the complete scheme for the formation of the six chlorobenzenes in question, a number of systems of electronic tautomerism are involved, but in the following abbreviated scheme III only those electronic formulæ have been included which are directly related to the present investigation, namely, the correlation of the molecular volumes of mono-, 1 . 2 di-, 1 . 2 4 or

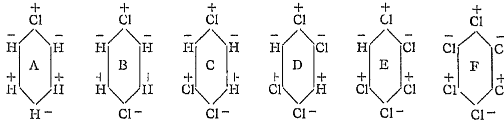
1 4 5 tri-, 1 2 4 5 tetra-, penta-, and hexa-chlorobenzenes with their respective electronic formulæ The electronic formulæ of these compounds are indicated in the following scheme III by the letters A, B, C, D, E, and F —

Scheme III



The scheme involves three systems of electronic tautomerism, namely, (A $\rightleftharpoons$ A′), (C $\rightleftharpoons$ C′), and (E $\rightleftharpoons$ E′) Beginning with benzene, each of the six successive chlorinations introduces only one positive substituent, $\overset{+}{\text{Cl}}$, as has been illustrated in preceding schemes I and II Note that A′, C′, and E′ (the respective electromers of A, C, and E) yield on chlorination B, D, and F, respectively. Compounds B, D, and F do not possess electromers because they contain an *even* number of *symmetrically* substituted chlorine atoms On the other hand, the electronic formulæ A, C, and E are in tautomeric equilibrium with their respective electromers A′, C′, and E′ since they embody an *uneven* number of substituted chlorine atoms and the number of their positive substituents is unequal to the number of their negative substituents.

Before tabulating the molecular volume data, it will facilitate comparisons if the electronic formulæ of the six chlorobenzenes are rewritten in juxtaposition and with the positive substituents in positions 1, 3, and 5, and the negative substituents in positions 2, 4, and 6. Such an arrangement will not alter in the least the electronic formulæ of these compounds as derived in the preceding scheme; the relative positions and polarities of the substituents remain the same.



C. The Molecular Volumes of the Chlorobenzenes.

The preceding arrangement of the electronic formulæ of the six chlorobenzenes (A-F) serves as a key to the following table of molecular volume values:—

Chlorobenzenes		V_m	V'_m	V_xCl	Δ
A Mono- .	(odd)	114·6	92·8	21·8	
					19·5
B 1, 4-Di-	(even)	130·9	89·6	41·3	
					21·4
C 1, 4, 5-Tri-	(odd)	149·1	86·4	62·7	
					18·9
D 1, 2, 4, 5-Tetra	(even)	164·8	83·2	81·6	
					22·3
E 1, 2, 3, 4, 5-Penta-	(odd)	183·9	80·0	103·9	
					19·3
F 1, 2, 3, 4, 5, 6-Hexa-	(even)	200·0	76·8	123·2	

The first column embodies the names of the six chlorobenzenes, A to F, inclusive. The designation (odd) or (even) refers to the number of chlorine atoms in the respective compounds. The former are unsymmetrical in structure, the latter, symmetrical. The molecular volumes of the chlorobenzenes, originally determined by Jungfleisch,[116] and subsequently retabulated by Le Bas, are given in the second column, V_m. The third column indicates the molecular volumes of the hydrocarbon groups of the compounds, V'_m. The difference between the molecular volume of a given chlorobenzene and its hydrocarbon group ($V_m - V'_m$) gives the molecular volume of its chlorine atoms, V_vCl, column four. The last column is one of differences (Δ) between the total volumes of the chlorine atoms of the successive compounds. For example, the atomic volume of the chlorine atom in mono-chlorobenzene is 21·8. The combined atomic volumes of the two chlorine atoms in 1 : 4 di-chlorobenzene is 41·3. The difference between these values, namely, 19·5, is, therefore, the volume of one chlorine atom while that of the other in the para position is 21·8. The electronic formula of benzene has shown that substituents para to each other are of opposite polarity. Since previous investigations have indicated that the positive chlorine atom may have a greater atomic volume than the negative chlorine atom, the correlation between the atomic volumes and the electronic formula is maintained in para-di-chlorobenzene. Further correlations are maintained throughout the series of the six chlorobenzenes since the column of differences (Δ) shows that the chlorine atoms successively substituted vary in their atomic volume values by an average difference of ± 2·6 units. This simultaneous variation in polarity and atomic volume is emphasized by the retabulations in the following table —

	Relative Position	Polarity	Atomic Volume (Positive)	Atomic Volume (Negative)
A 1st chlorine atom	(1)	(+)	21·8	—
B 2nd " "	(4)	(−)	—	19·5
C 3rd " "	(5)	(+)	21·4	—
D 4th " "	(2)	(−)	—	18·9
E 5th " "	(3)	(+)	22·3	—
F 6th " "	(6)	(−)	—	19·3
	Mean values		21·8	19·2
			Δ = 2·6	

It is, therefore, evident that a marked difference (average Δ = 2·6) exists between the atomic volumes of the chlorine atoms in positions 1, 3, and 5 and those in positions 2, 4, and 6, and, since the electronic formula of benzene and the substitution rule has shown that substituents in positions 1, 3, and 5 are opposite in polarity to those in positions 2, 4, and 6, it follows that *a definite relationship exists between the electronic formulæ of the six chlorobenzenes and their respective molecular volumes. The existence of this relationship may be regarded as* *additional evidence, from a physical point of view, for the electronic formula of benzene.*

Various facts presented in this chapter seem to indicate that a change in the polarity of a halogen atom causes a variation in its atomic volume. Any attempts to explain this in the present state of our knowledge would plunge us fatally into the metaphysics of an atomic structure maelstrom. Notwithstanding the incomplete knowledge of the constitution of the atom as manifested by the many different hypotheses relative to the nature and disposition of "valence electrons," it is quite conceivable that variations in *the relative positions of the valence electrons which determine the polarity of an atom may likewise cause variations in the atomic volume of the atom.* This assumption may lead to an explanation of other anomalies in molecular volume relationships. For instance, in the compounds methylene dichloride, chloroform, and carbon tetrachloride, previously noted, the average atomic volumes of the chlorine atoms are 21·5, 22·0, and 22·2, respectively. This small increase in the average volumes of the chlorine atoms as they accumulate about a given carbon atom may be due to the relative positions of the valence electrons between the carbon and chlorine atoms which may mutually alter the respective atomic volumes of these atoms. It has also been noted that for one substitution in the β-position of a compound the contraction in molecular volume is a little over three units while substitutions on the γ- and δ-positions result in even greater contractions. These anomalies may also be related to differences in the relative positions of the valence electrons between the carbon atoms and the halogen atoms substituted in the α-, β-, γ-, and δ-positions, thus causing varying differences in the degrees of contractions.

In conclusion, a quotation from Le Bas should be noted:—

"There is no doubt that in spite of the care taken, many parts of the present theory of molecular volumes may have to be altered later as data accumulate, and as our knowledge of the physical property increases. The identification and explanation of constitutive effects is not always easy. Some particular atomic values—generally those found in the homologous series R—X are taken as standard, and by the method of summation the value ΣnV_a is found. The difference, $V_m \Sigma nV_a$, then measures the constitutive effect. Sometimes a mean atomic value is taken, and it then follows that no account is taken of variations The great difficulty is to identify the effect with a particular atom or group When this seems possible, it sometimes happens that other atoms or groups might equally well be identified with the effect in question Only a careful examination of a large number of data can overcome these difficulties It will generally be found that the constitutive effects are traceable to some modifications in particular atomic values, and a considerable advance is made when we are able to ascertain for certain which atoms are marked by the variation in question and by how much "

Apropos of the above quotation, and as a summary of the present chapter, it has been shown that —

(1) Halogen atoms which function positively appear to possess different atomic volumes from those which function negatively Consequently, it is possible to correlate certain additive and constitutive effects apparent in the molecular volumes of certain compounds with their electronic formulæ These effects cannot be explained by means of the ordinarily employed structural formulæ

(2) Definite relationships exist between the molecular volumes of six different chlorobenzenes and their respective electronic formulæ These relationships further confirm the electronic formula of benzene

(3) It is suggested that any variations in the relative positions of the valence electrons which determine the polarity of an atom may likewise cause variations in the atomic volume of the atom

CHAPTER XVIII

DYNAMIC FORMULÆ AND THE ULTRAVIOLET ABSORPTION SPECTRUM OF BENZENE

A. Colour in Relation to Chemical Constitution.

IT is the purpose of this chapter to present the development of a relationship, in the nature of a linear function, between the systems of dynamic equilibria of the various electromers of benzene and the oscillation frequencies of the seven bands which characterize the ultraviolet absorption spectrum of benzene solutions The existence of such a relationship would not only further substantiate the electronic formulæ of benzene but also afford a new explanation of colour in relation to chemical constitution

Watson,[116] in the preface to his recent monograph, "Colour in Relation to Chemical Constitution," states that "the early theories as to the relation between colour and constitution, such as the quinonoid theory and Nietzki's rule, have proved of great value for practical purposes, viz, in the production of dyestuffs and especially for the preparation of dyestuffs of any required shade, but more recent researches have shown that these classical theories are by no means adequate Modified and new theories have been proposed which agree better with the known facts The quest of the *ultimate cause of colour* has revealed *the great complexity of the problem* and has shown the need for further work in this direction"

The fundamental cause of the absorption of light by benzene, as proposed in this chapter, is necessarily complex since it has to deal with the somewhat complicated systems of dynamic equilibria of the electromers of benzene. But if the absorption of light of known oscillation frequency can be correlated with the electronic formulæ of benzene, then it may be concluded that some definite advance has been made in the quest of the ultimate cause of colour in its relation to chemical constitution

B. The Systems of Dynamic Equilibria of the Electromers of Benzene.

A statement made by Stewart[117] should be recalled at this point "It is becoming generally recognized that the benzene molecule is in a state of continual vibration, and that the only satisfactory space formula will be one which represents all the other formulæ as phases of its own motions, *and which may even suggest the possibility of new phases as yet unrecognized* The main outlines of such a formula have been indicated by Collie, and it seems probable that any space formulæ of benzene which may be proposed in the future will agree with his in essentials"

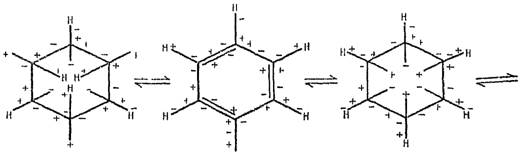
The plane projections of Collie's space formulæ and the twofold movements which are attributed to the system have been described and illustrated in Chapter VII., Section B (p 48) Collie's space formulæ are correlated readily with the Kekulé and centric formulæ since, through their movements, they are mutually interconvertible

Again, recall that a complete application of the electronic conception of positive and negative valences to the benzene molecule, involves five types of carbon atoms, namely,

$$\begin{array}{ccccc} +\ + & -\ + & -\ + & -\ + & -\ - \\ \mathrm{C} & \mathrm{C} & \mathrm{C} & \mathrm{C} & \mathrm{C} \\ +\ + & +\ + & -\ + & -\ - & -\ - \\ \mathrm{I} & \mathrm{II} & \mathrm{III} & \mathrm{IV} & \mathrm{V} \end{array}$$

and if benzene nuclei (centric formulæ) are composed of these several types, each nucleus consisting of three pairs of the combined types I and V, II and IV, and III. and III, symmetrically co-ordinated, six and only six centric electronic formulæ (electromers) are possible, as previously shown in Chapter VII

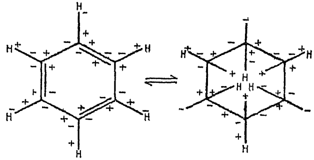
Now, if in place of the one centric phase of Collie's space formulæ, there be six centric electromers, then there will be six times as many Kekulé and other phases in a complete system of dynamic equilibria of the electromers of benzene Before this extended system is developed, consider specifically the plane projections of those electromers that are related to the centric formula which is composed of carbon atoms of type III —



First phase

First Kekulé phase

Centric phase



Second Kekulé phase

Last phase

Note that the first and second Kekulé phases present two distinct types of double bonds. In the former, each of the two bonds (Faraday tubes) comprising a double bond has the same direction, since their adjacent ends are of the same sign or polarity. In the latter, the bonds have opposite direction, since their adjacent ends are of opposite sign or polarity. Hence these two types of double bonds may be designated by the terms *diplex* and *contraplex* respectively.

In the complete scheme of dynamic equilibria of the electromers of benzene, presented in Fig. 1, p. 188, the first and last phases, which are respectively related to the first and second Kekulé phases, have been omitted for the sake of brevity. The centric electromer A, the starting-point of the scheme, so to speak, is composed of carbon atoms of the types I and V. Electromer A functions as the intermediate phase between A′ and A″.

Kekulé held that the atoms of carbon oscillate in the molecule of benzene in such a way that A′ would represent the constitution of the molecule at one period of oscillation, and A″ the constitution at another period. This conception introduces a kind

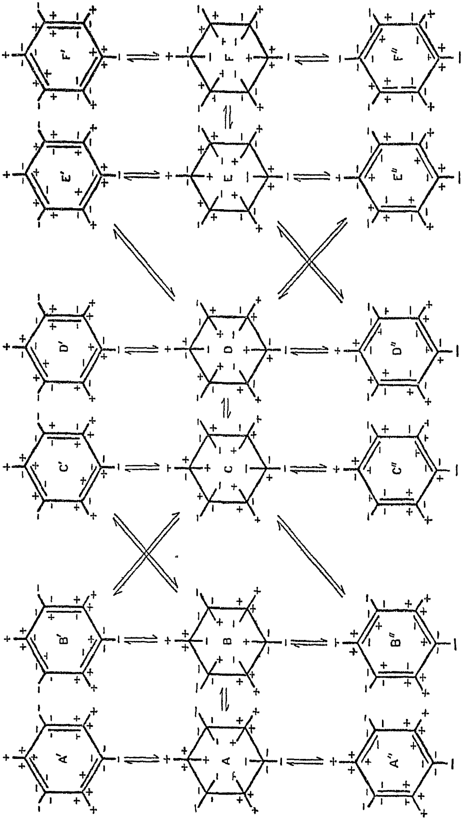


FIG 1 —Scheme of dynamic equilibria of the electromers of benzene

of structural modification differing both from ordinary isomerism and tautomerism for which Bruhl[118] has suggested the term *phasotropism*, in the sense that "the *unaltered* benzene nucleus and analogous ring systems are phasotropic." On the electronic basis, A′ and A″ may be termed *phasotropic electromers*, neither of which could revert to the centric electromer A, unless there was a rearrangement of bonds or Faraday tubes. Such a change would result in another state of equilibrium in the centric electromer or phase.

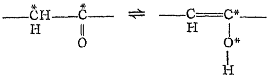
Faraday introduced the term "dielectric polarization" to describe the condition of a non-conductor or dielectric, as he conceived it, when in a state of *strain* under the action of two adjacent charges of positive and negative electricity, as, for example, in the condenser. Accordingly, the centric phase may be assumed to present a state of strain, or of meta-stable equilibrium, by virtue of the balance between three positive and three negative charges within the ring; hence it may be said to be in a condition of dielectric polarization. The rearrangement of the three positive and three negative charges of the centric electromer in such a manner that the positive charges occupy the positions antecedently held by the negative charges, and vice versâ, produces at one and the same time not only a similar condition of dielectric polarization, but also another centric electromer. Thus, the centric electromer A composed of carbon atoms of the types I and V undergoes *centric rearrangement* yielding another centric electromer B composed of carbon atoms of the types II and IV. There are three distinct centric rearrangement equilibria, or transitions, in the complete scheme, namely, $A \rightleftharpoons B$, $C \rightleftharpoons D$, $E \rightleftharpoons F$. Note that centric rearrangement is structurally impossible between B and C, and between D and E.

In Collie's space formulæ for benzene, the centric phase is intermediate between two, and only two, Kekulé or phasotropic phases. In the proposed scheme, *in which every electronic formula is the plane projection of a space formula*, a given centric electromer may be the intermediate phase between two, three, or four phasotropic electromers. For example, A is the intermediate phase between A′ and A″; B, between B′, B″, and C′; C, between B′, B″, C′, and C″. Note that the transition from B to C may be effected through B′, B″, or C′, but not through C″; also, the transition from D to E may be effected through E′, E″, and D″, but not through D′ In this manner the inter-relations of the eighteen electromers comprising the complete scheme of equilibria may be readily traced.

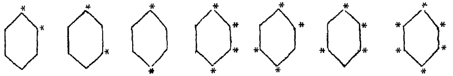
The scheme as thus outlined, presents, when considered dynamically, two types of dynamic equilibria which shall be designated as *primary* and *secondary systems* of phasotropic equilibria. A primary system or transition involves three phases namely, one centric electromer and any two of its directly related phasotropic electromers, as for example, the transitions $A' \rightleftharpoons A \rightleftharpoons A''$, $B' \rightleftharpoons B \rightleftharpoons B''$, or $B' \rightleftharpoons C \rightleftharpoons C''$ A secondary system or transition involves four phases, namely, two centric electromers, which are interconvertible by centric rearrangement, and one phasotropic electromer of each of the two interconvertible centric electromers, as for example the transitions of $A' \rightleftharpoons A \rightleftharpoons B \rightleftharpoons B'$, or $B' \rightleftharpoons C \rightleftharpoons D \rightleftharpoons E''$ Twenty primary transitions and twenty-eight secondary transitions are embodied in the complete scheme They will be tabulated and discussed later

The possibility of correlating these various electromers and their systems of dynamic equilibria with the oscillation frequencies of the seven bands of the absorption spectrum of benzene constitutes the present problem Baly and Desch[119] maintain that the benzene absorption bands are to be accounted for by the synchronous oscillations of the benzene molecule in some such way as a tuning-fork vibrates in response to a note of definite pitch In terms of the electron theory, they state that "combination between two atoms is accompanied by the passage of one or more electrons from one atom to the other producing one or more Faraday tubes of force between them, each Faraday tube representing the chemists' single bond If by some means we cause the rearrangement of these linkings or Faraday tubes, it is clear that there must occur a vibrational disturbance in the systems of electrons of the atoms concerned Now we have direct evidence of these disturbances in the fluorescence of tautomeric substances as shown by Hewitt[120] It is, therefore, only natural that the converse takes place, namely, the absorption of light by tautomeric substances."

Baly and Desch show that this process in the aliphatic compounds involves the make and break between a carbon and an oxygen atom, thus—



the stars being attached to those atoms which are undergoing the linking change Compounds which manifest keto-enol tautomerism display an absorption band Applying this idea to benzene, Baly and Collie[121] differentiate between the transition phases in which any pair of carbon atoms, or any four, or all six are concerned, the various transition phases being represented as follows —



These seven forms are held to represent all the possible conditions of making and breaking the linkings which can occur, each *per se* being the origin of a separate absorption band.

This hypothesis of Baly and Collie does not offer any definite explanation as to how the seven phases of benzene may be brought about, apart from being the result of some form of motion of the atoms in the molecules. Moreover, since it does not attribute or relate any one of the above seven phases to any one of the seven absorption bands, it thereby fails to indicate any possible numerical relationship between the various phases and the oscillation frequencies of the seven bands An hypothesis designed to meet these deficiencies is offered in the following paragraphs

C. The Electronic Interpretation of Keto-Enol Tautomerism in relation to the Absorption of Light.

Accepting the finding of Baly and Desch that an absorption band is the result of coexistent ketonic and enolic forms in dynamic equilibria, three questions arise —

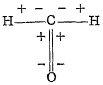
(1) What is the significance of the keto-enol condition of dynamic equilibrium from the standpoint of the *electronic formulæ* of keto-enol compounds?

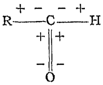
(2) Is this significance common both to the keto-enol systems

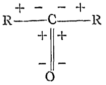
of dynamic equilibria and to the primary and secondary systems of phasotropic equilibria of the electromers of benzene?

(3) How are the systems of phasotropic equilibria to be correlated (*a*) with the existence of seven bands in the absorption spectrum of benzene, and (*b*) with the oscillation frequencies of each of the seven bands? The following answers are proposed —

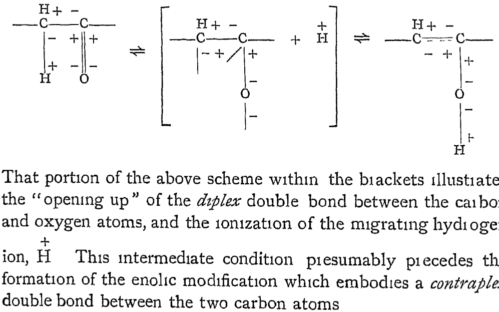
(1) The electronic formulæ of ketonic and enolic modifications are derivable from the electronic formula of one of the five typical compounds (see Chapter III, Section B, p 17), namely, formaldehyde The formula of an aldehyde or of a ketone is indicated by replacing one or two hydrogen atoms, respectively, of formaldehyde by alkyl radicals —


Formaldehyde


An Aldehyde


A Ketone.

Keto-enol tautomerism involves the migration to and fro of a hydrogen atom between carbon and oxygen atoms Having indicated the electronic formula of a ketone, the keto-enol tautomeric equilibrium may be represented electronically as follows —



That portion of the above scheme within the brackets illustrates the "opening up" of the *diplex* double bond between the carbon and oxygen atoms, and the ionization of the migrating hydrogen ion, $\overset{+}{H}$ This intermediate condition presumably precedes the formation of the enolic modification which embodies a *contraplex* double bond between the two carbon atoms

Note particularly that the rearrangement of valences or Faraday tubes involves a change in the nature or type of double bonds as found in the keto- and enol-forms The former presents a *diplex* double bond between the carbon and the oxygen atom, the latter, a *contraplex* double bond between the two carbon atoms Hence the electronic significance of the keto-enol transition resolves itself to a condition of dynamic equilibrium involving transition from diplex to contraplex double bonds and vice versâ Systems of dynamic equilibria involving changes from diplex to contraplex double bonds and vice versâ, will be termed *contraplex-diplex transitions.* This disposes of the first question

(2) With reference to the second question, the hypothesis now proposed does not limit contraplex-diplex transitions to keto-enol tautomerism, but further assumes that the occurrence of *contraplex-diplex transitions in any types of dynamic equilibria constitutes the structural and the electronic explanation of absorption bands, that is, of colour* The occurrence of these transitions among the primary and secondary systems of phasotropic equilibria of the electromers of benzene have been noted, hence, they naturally constitute the basis of the explanation of the absorption spectrum of benzene. The discussion of the third question now follows

Since there are seven absorption bands in the benzene spectrum, and it is assumed that the transition from contraplex to diplex bonds and vice versâ, is the electronic explanation of an absorption band, then there must be seven such distinct systems involved in the complete scheme of phasotropic equilibria A tabular arrangement (see next page), (cf Fig 1, p. 188) of all the possible primary and secondary systems of phasotropic equilibria presents twenty of the former and twenty-eight of the latter

The electromers containing diplex bonds are A′, A″, C″, D′, F′, and F″, while those containing contraplex bonds are B′, B″, C′, D″, E′, and E″ Only those equilibria, either primary or secondary, which involve transitions from an electromer containing diplex to one containing contraplex bonds, or vice versâ, are followed by asterisks. These only may function as the origin of the absorption bands.

Since six centric electromers figure in the complete scheme of equilibria, there are, accordingly, six classes of primary transitions, each class involving one centric phase Only six of the twenty primary transitions are asterisked, namely, those

Primary Systems of Phasotropic Equilibria

{ 1 A′—A—A″

2 B′—B—B″

3 B′—B—C′
4 B″—B—C′

5 B′—C—B″

6 B′—C—C′
7 B″—C—C′
8 B′—C—C″ * } α
9 B″—C—C″ *

10 C′—C—C″ * } β

11 D′—D—D″ * } γ

12 D′—D—E′ * } δ
13 D′—D—E″ *
14 D″—D—E′
15 D″—D—E″

16 E′—D—E″

17 E′—E—E″
18 E′—E—D″
19 E″—E—D″

{20 F′—F—F″

Secondary Systems of Phasotropic Equilibria

1 A′—A—B—B′ * } I
2 A′—A—B—B″ *
3 A″—A—B—B′ *
4 A″—A—B—B″ *

5 A′—A—B—C′ * } II
6 A″—A—B—C′ *

7 B′—C—D—D′ * } III
8 B″—C—D—D′ *
9 B′—C—D—D″
10 B″—C—D—D″

11 B′—C—D—E′
12 B′—C—D—E″
13 B″—C—D—E′
14 B″—C—D—E″

15 C′—C—D—D′ * } IV
16. C′—C—D—D″
17 C″—C—D—D′
18 C″—C—D—D″ *

19 C′—C—D—E′
20 C′—C—D—E″
21 C″—C—D—E′ * } V
22 C″—C—D—E″ *

23 D″—E—F—F′ * } VI
24 D″—E—F—F″ *

25 E′—E—F—F′ * } VII
26 E′—E—F—F″ *
27 E″—E—F—F′ *
28 E″—E—F—F″ *

numbered 8 to 13 inclusive, which in turn are subdivided into four distinct groups as follows —

Group (α) 2 transitions, numbered 8 and 9,
,, (β) 1 transition, ,, 10,
,, (γ) 1 ,, ,, 11,
,, (δ) 2 transitions, ,, 12 and 13

Since the complete scheme involves three centric rearrangements, $A \rightleftharpoons B$, $C \rightleftharpoons D$, and $E \rightleftharpoons F$, there are accordingly three classes of secondary transitions They are numbered 1 to 6, 7 to 22, and 23 to 28 inclusive, respectively Eighteen of the twenty-eight secondary transitions are asterisked and fall naturally into *seven* distinct groups as follows —

Group I 4 transitions, numbered 1 to 4 inclusive,
,, II 2 ,, ,, 5 and 6,
,, III 2 ,, ,, 7 ,, 8,
,, IV 2 ,, ,, 15 ,, 18,
,, V 2 ,, ,, 21 ,, 22,
,, VI 2 ,, ,, 23 ,, 24,
,, VII 4 ,, ,, 25 to 28 inclusive

An eighth group, transitions 11 to 14 inclusive, does not embrace any contraplex-diplex equilibria, consequently, it plays no part in the development of the present hypothesis.

D. The Correlation of Oscillation Frequencies and Contraplex-Diplex Transitions.

The existence of *seven distinct groups of secondary contraplex-diplex systems of equilibria* constitutes the basis of the correlation of the *seven absorption bands* of benzene The oscillation frequencies of the heads of these bands as determined by Baly and Collie are as follows ·—

Band	Oscillation Frequency
One	3725
Two	3765
Three	3830
Four	3915
Five	4025
Six	4110
Seven	4200

In attempting to correlate the seven groups of secondary contraplex-diplex equilibria with the above oscillation frequencies, let it be assumed that the *number* of transitions in each of the seven groups functions successively and collectively in the production of the seven bands Naturally *two*, the smallest number of secondary transitions contained in a single group, may then be assumed to function in the production of the band of *lowest* frequency, namely, band One, 3725. On the other hand, since there are altogether twenty-four contraplex-diplex transitions in the complete system, it may likewise be assumed that all of these function in the production of band Seven of highest frequency, 4200. In other words, the vibrations of two secondary contraplex-diplex transitions are synchronous with light waves of frequency 3725 , while the vibrations of twenty-four (i.e , eighteen secondary plus six primary) contraplex-diplex transitions are synchronous with light waves of frequency 4200

These assumptions relative to the origin of bands One and Seven are of no merit or value unless some means is at hand of determining the numbers of transitions involved in the production of each of the five remaining bands. Furthermore, these numbers must be whole numbers since the present hypothesis requires that they be the sums of the transitions in the secondary groups I. to VII. inclusive, and the transitions in the primary groups,

α, β, γ, and δ In other words, a linear function must be shown to exist between the oscillation frequency of each of the seven bands and an *integral number* of contraplex-diplex transitions The possibility that the frequencies of the absorption bands of benzene are a function of a series of whole numbers is suggested by the discovery of Balmer,[122] that the wave-lengths of the lines in the hydrogen spectrum are a function of successive whole numbers. His formula,

$$\lambda = h\frac{m^2}{m^2 - 4} \quad 10^{-6},$$

in which $h = 3646\ 13$, and m is given the values 3, 4, 5, 6, etc , is only one of several showing the existence of similar series in the line spectra of various elements

A similar relationship becomes apparent if the oscillation frequency 3725 (band One) involving two transitions and 4200 (band Seven) involving twenty-four transitions serve as two points in a system of rectangular co-ordinates , namely (3725, 2) and (4200, 24) The calculated equation for a straight line passing through these two points is $y = 21\ 591x + 3681\ 818$ in which (y) is the oscillation frequency of a given band and (x) is the number of contraplex-diplex transitions functioning as the origin of the given band Assuming on the one hand that the frequencies (y) as determined by experimental observation are absolutely correct, the corresponding numbers of transitions (x) involved therein may be calculated On the other hand, employing as values for (x) those whole numbers which are most closely approximated by the previously calculated values of (x), the corresponding values of (y) may in turn be ascertained Thus theoretical and actual values may be compared. In Table No 1—

TABLE No 1

($y = 21\ 591x + 3681\ 818$)

A	B	C (A - B)	D	E	F (D - E)
2 000	2	0 000	3725	3725 000	0 000
3 853	4	− 0 147	3765	3768 181	− 3 181
6 863	7	− 0 137	3830	3832 954	− 2 954
10 800	11	− 0 200	3915	3919 318	− 4 318
15 895	16	− 0 105	4025	4027 272	− 2 272
19 832	20	− 0 168	4110	4113 636	− 3 636
24 000	24	0 000	4200	4200 000	0 000

column A contains the calculated values for (x), column B, the series of whole numbers most nearly approximated by the calculated values of column A, column C, the differences between values in columns A and B, column D, the oscillation frequencies as experimentally determined by Baly and Collie, column E, the calculated frequencies (y) corresponding to the assumed whole number values for (x) in column B, column F, the differences between the actual frequencies in column D and the calculated frequencies of column E

The values in column A approximate very closely the whole numbers in B as is evidenced by the column of differences, C This favours the assumption that *the oscillation frequencies are a function of whole numbers* Furthermore, the frequencies in column D calculated upon this assumption approximate the actual frequencies in column E as is evidenced by the column of differences F, which are practically within the limits of error of experimental observation.

The calculated values of Table No. 1 are based upon the assumption that the frequencies of bands One and Seven are absolutely correct while the frequencies of the intermediate bands were not considered in determining the equation of the line relating frequencies and the numbers of contraplex-diplex transitions. Numerical values of greater significance are to be found in another equation, namely, $y = 21{\cdot}6063x + 3679{\cdot}296$, which is derived by an application of *the method of least squares to the whole numbers* (x) *and the actual oscillation frequencies* (y) taken from columns A and D of Table No 2

TABLE No 2

($y = 21{\cdot}6063x + 3679{\cdot}296$.)

A	B	C (B − A)	D	E	F (D − E)
2	2·115	+ 0·115	3725	3722 509	+ 2 491
4	3·966	− 0·034	3765	3765 721	− 0 721
7	6 975	− 0 025	3830	3830 540	− 0 540
11	10·909	− 0 091	3915	3916·965	− 1 965
16	16·000	0·000	4025	4024 996	+ 0 004
20	19·934	− 0 066	4110	4111·421	− 1 421
24	24·099	+ 0·099	4200	4197 847	+ 2 153

The deviations, column C, of the calculated numbers, column B, from the assumed whole numbers, column A, are so slight as fully to warrant the assumption that the oscillation frequencies of the seven bands, column D, are a linear function of the corresponding whole numbers, column A, which are the numbers of the contraplex-diplex transitions involved therein. This hypothesis is further substantiated in that the deviations, column F, from the experimentally determined values, column D, are well within the limits of error of experimental observation. The *probable error* in the value of any of the oscillation frequencies, as calculated by Peters' formula, is only 1 328

This remarkable relationship between the series of seven whole numbers and the oscillation frequencies of the seven absorption bands of benzene (columns A and D respectively of Table No 2) is graphically illustrated in Fig 2. The seven whole numbers (X-axis) and the corresponding oscillation frequencies (Y-axis) permit the location of seven points in the system of rectangular co-ordinates A line drawn through each of these seven points is practically a straight line This, in conjunction with the data of preceding Tables 1 and 2, both warrants and substantiates the hypothesis that the oscillation frequencies of the heads of the absorption bands of benzene are a linear function of the numbers of contraplex-diplex transitions involved in the system of dynamic equilibria of the electromers of benzene

E. The Origin of Each Absorption Band.

One other question remains to be considered, namely, that of the possibility of relating each of the seven absorption bands to its proper source It has been assumed that the vibrations of two secondary contraplex-diplex transitions are synchronous with light waves of frequency 3725 (band One) while the vibrations of twenty-four, i e, the eighteen secondary and the six primary contraplex-diplex transitions, are synchronous with light waves of frequency 4200 (band Seven) The intervening whole numbers, 4, 7, 11, 16, and 20, represent the numbers of transitions similarly involved in the production of bands Two, Three, Four, Five, and Six, respectively Of the seven distinct groups of secondary phasotropic equilibria, one and only one group of transitions is related to band One These *two* transitions of one group plus *two* transitions of one other of the seven groups gives *four* which are related to band Two In turn, these *four* plus *three* other transitions gives *seven* which are related to band Three. In this manner the entire series of whole numbers,

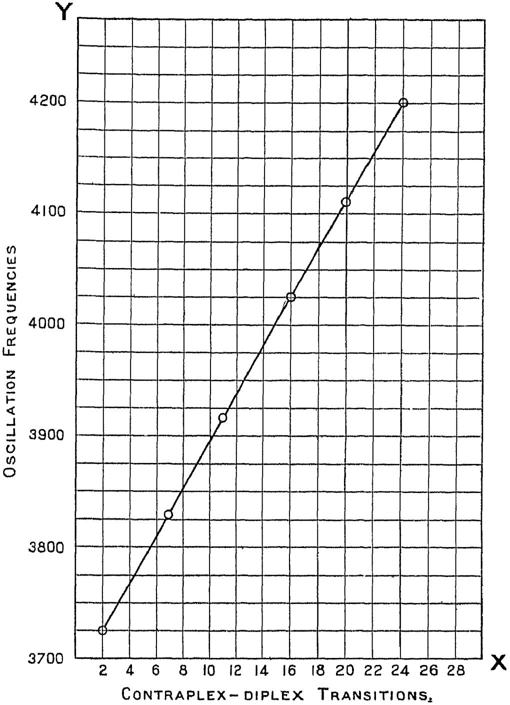


FIG. 2.—Benzene in Alcohol (Baly).

2, 4, 7, 11, 16, 20, 24 may be built up, *but each increment in the series must involve the addition of the transitions of one and only one of the seven groups of secondary contraplex-diplex equilibria,* *while one or more of the primary groups may or may not be added* This condition preserves the correlation of the seven groups of secondary phasotropic equilibria with the seven bands in a consistent and symmetrical manner

The following scheme embodies such an arrangement of the several groups of transitions, and should be studied in conjunction with the tables of primary and secondary phasotropic equilibria and the complete system of the electromers of benzene in dynamic equilibria. The groups of secondary equilibria are designated by the Roman numerals I to VII. inclusive and the primary equilibria by the letters α, β, γ, and δ, while the subscript numeral is the number of transitions involved in the given group For example, (IV_2) signifies the two secondary contraplex-diplex transitions, namely, $C' \rightleftharpoons C \rightleftharpoons D \rightleftharpoons D'$ and $C'' \rightleftharpoons C \rightleftharpoons D \rightleftharpoons D''$, of group IV , ($\beta_1$) signifies the one primary contraplex-diplex transition, namely, $C' \rightleftharpoons C \rightleftharpoons C''$, of group β. The symmetrically evolved scheme relating each of the seven absorption bands to its possible source is as follows —

Band	Origin	Number of Transitions Involved
One	IV_2	2
Two	$IV_2 + (III_2 \text{ or } V_2)$	4
Three	$IV_2 + III_2 + V_2 + (\beta_1 \text{ or } \gamma_1)$.	7
Four	$IV_2 + III_2 + V_2 + (\beta_1 \text{ or } \gamma_1) + (II_2 \text{ or } VI_2) + (\alpha_2 \text{ or } \delta_2)$ . .	11
Five	$IV_2 + III_2 + V_2 + \beta_1 + \gamma_1 + II_2 + VI_2 + \alpha_2 + \delta_2$	16
Six	$IV_2 + III_2 + V_2 + \beta_1 + \gamma_1 + II_2 + VI_2 + \alpha_2 + \delta_2 + (I_4 \text{ or } VII_1)$	20
Seven	$IV_2 + III_2 + V_2 + \beta_1 + \gamma_1 + II_2 + VI_2 + \alpha_2 + \delta_2 + I_4 + VII_1$	24

Note that the transitions of group IV. involve the centric electromers C and D which constitute the nucleus, so to speak, of the complete system of dynamic equilibria of the electromers of benzene Accordingly, the other groups of transitions are successively and collectively embraced, producing in a natural sequence the series of seven whole numbers which are functions of the oscillation frequencies of the seven bands, and which represent the number of specifically indicated contraplex-diplex transitions involved in the production of each band respectively.

The conception that contraplex-diplex transitions occasion the absorption of light in carbon compounds is extended, in the next two chapters, to the dynamic formulæ and the absorption spectra of chlorobenzene, bromobenzene, and naphthalene, with the uniform result that the oscillation frequencies of the absorption bands are functions of the numbers of contraplex-diplex transitions involved in the systems of dynamic equilibria of their electromers

CHAPTER XIX

ABSORPTION SPECTRA AND DYNAMIC ELECTRONIC FORMULÆ OF CHLORO-, BROMO-, AND IODO-BENZENE

THE purpose of the present chapter is to test the validity of the absorption theory (just developed in relation to benzene) by extending it to the ultraviolet absorption spectra of chloro- and bromobenzenes In this connection, the non-selective absorption of iodobenzene requires an explanation

The existence of a rule has been indicated This rule, a linear relationship ($y = sx + b$), involves definite numbers (x) of contraplex-diplex transitions occurring within the systems of phasotropic equilibria of the electromers of the compound, and the oscillation frequencies (y) of its absorption bands In this and subsequent chapters, contraplex-diplex transitions will be termed *absorption transitions* In other words it will be maintained that the oscillation frequency (y) of the head of a given band is a linear function of the number of absorption transitions (x) which function as the origin of the band of frequency (y)

Purvis[123] undertook the investigation of the absorption spectra of chloro-, bromo-, and iodobenzenes in order to ascertain (1) the nature of the absorption of the radiant energy, and (2) how far the displacement of one atom of hydrogen of benzene by chlorine, bromine, or iodine, affects the type of absorption when the compounds were in the vapour state, in solution in alcohol, or in very thin films Therefore, the present chapter is limited to a discussion of the effect of the displacement of one hydrogen atom of the benzene molecule, by the halogens noted above, upon the absorption spectra of the compounds *in solution* (*a*) in alcohol, and (*b*) in thin films. The purpose of the present development is threefold —

(1) To compare the data of Purvis with the data of Baly concerning the oscillation frequencies of the absorption bands of chlorobenzene when dissolved in alcohol.

(2) To compare and interpret the differences in the values of the oscillation frequencies (according to Purvis) of the absorption

bands of chlorobenzene and bromobenzene under different physical conditions, namely (*a*) when the substances are dissolved in alcohol, and (*b*) when the substances are in the form of very thin films.

(3) To present a new explanation of the non-selective absorption of iodobenzene.

Purvis[124] found that alcoholic solutions of chlorobenzene and bromobenzene of equimolar concentrations, through equal thicknesses, exhibit *seven* wide diffuse bands which are comparable in appearance, and are shifted a little more towards the less refrangible end of the spectrum in the bromobenzene solution. Purvis thus demonstrated that the earlier investigations of Baly and Collie,[125] and Baly and Ewbank,[126] were incomplete because they failed to locate and determine the positions of the entire seven bands of these compounds. Subsequently, Baly[127] again undertook the investigation of the absorption spectra of chlorobenzene and found *seven* bands, the same number previously established by Purvis. The positions of the heads of the bands, as determined by Purvis in wave-length values (λ), have been converted in the present discussion to the corresponding values in oscillation frequencies (1/λ) so that comparisons may be made readily with the data of Baly, originally given in oscillation frequencies. Furthermore, it is an advantage to have all data recorded in oscillation frequencies since the rule under consideration states that the *oscillation frequencies are linear functions of the absorption transitions*.

The following Table I. includes the oscillation frequencies of the absorption bands of benzene, chlorobenzene, and bromobenzene in alcoholic solution; and chlorobenzene and bromobenzene in very thin films. Iodobenzene shows no absorption bands.

TABLE I.

Number of Band.	$C_6H_5 . H$ Solution (Baly).	$C_6H_5 . Cl$ Solution (Baly).	C_6H_5 Cl Solution (Purvis)	C_6H_5 Br Solution (Purvis)	C_6H_5 Cl in Films (Purvis).	C_6H_5 Br in Films (Purvis)
One	3725	3682	3685	3679	3674	3670
Two	3765	3777	3781	3775	3772	3768
Three .	3830	3825	3814	3821	3818	3815
Four	3915	3878	3880	3874	3871	3868
Five	4025	3920	3923	3917	3912	3909
Six	4110	3975	3984	3976	3974	3971
Seven .	4200	4072	4082	4073	4054	4049

An inspection of the above table shows that chlorobenzene and bromobenzene either in alcoholic solution or in thin films display the same number of absorption bands as does benzene, namely, seven. Furthermore, the regions of selective absorption of these compounds are not widely different. These facts lead to the conclusion that the absorption transitions which constitute the origin of the seven absorption bands of benzene must function similarly as the origin of the seven absorption bands of chlorobenzene and of bromobenzene. Therefore, before considering in detail the origin of the absorption bands of chlorobenzene and bromobenzene, it will be necessary to recall briefly the relationship between the oscillation frequencies of the seven bands of benzene and the numbers of absorption transitions which are presented by its electromers in dynamic equilibria.

Within the complete scheme of dynamic equilibria of the electromers of benzene (see Fig. 1, p. 188) there are involved altogether twenty primary systems and twenty-eight secondary systems of phasotropic equilibria. All of these transitions are tabulated on page 194, but it is more convenient in the present chapter to refer to the following abbreviated Table II. which embodies only those transitions which function in the absorption of light, namely, the contraplex-diplex or absorption transitions. These are indicated as groups I. to VII. and groups α, β, γ, and δ.

TABLE II

I	A'—A—B—B' A'—A—B—B'' A''—A—B—B' A''—A—B—B''
II	A'—A—B—C' A''—A—B—C'
III	B'—C—D—D' B''—C—D—D'
IV	C'—C—D—D' C''—C—D—D''
V	C''—C—D—E' C''—C—D—E''
VI.	D''—E—F—F' D''—E—F—F''
VII	E'—E—F—F' E'—E—F—F'' E''—E—F—F' E''—E—F—F''
α	B'—C—C'' B''—C—C''
β	C'—C—C''
γ	D'—D—D''
δ	D'—D—E' D'—D—E''

A mathematical relationship between various groups or numbers of these absorption transitions and the oscillation frequencies of the seven absorption bands of benzene was developed by means of the system of rectangular co-ordinates in section D of Chapter XVIII.

Before extending this method of deriving the series of numbers of absorption transitions to chlorobenzene and bromobenzene, it should be observed that each of these compounds is a mono-substituted derivative of benzene and the substituents, chlorine and bromine, are saturated atoms possessing neither free nor latent valences which might interfere in some manner with the centric valences of the benzene nucleus Therefore, it is reasonable to assume further that the benzene nucleus in chlorobenzene and in bromobenzene is capable of undergoing the same *centric-rearrangements*[128] that are characteristic of benzene itself. Accordingly, chlorobenzene and bromobenzene would likewise present within the scheme of dynamic equilibria of their electromers the same total number of absorption transitions that are common to benzene, namely, twenty-four. Hence the scheme of transitions for benzene indicated in Table II (p 204) and Fig. 1 (p. 188) will apply equally to chlorobenzene and bromobenzene in the following discussion

A. The Absorption Spectrum of Chlorobenzene in Alcoholic Solution.

In the following Table III the oscillation frequencies of the absorption bands of chlorobenzene in alcoholic solution (as separately determined by Baly and by Purvis) and their respective successive differences are indicated There is also included for subsequent reference a third column containing the frequencies of the bands of bromobenzene and their successive differences, the observations being made upon the compound in alcoholic solution —

TABLE III

Number of Band.	C_6H_5Cl (Baly)	Difference	C_6H_5Cl (Purvis)	Difference	C_6H_5Br (Purvis)	Difference
One	3682		3685		3679	
		95		96		96
Two	3777		3781		3775	
		48		33		46
Three	3825		3814		3821	
		53		66		53
Four .	3878		3880		3874	
		42		43		43
Five	3920		3923		3917	
		55		61		59
Six	3975		3984		3976	
		97		98		97
Seven	4072		4082		4073	

The columns of differences show that the greatest discrepancies occur in the frequencies of bands Three, Six, and Seven These differences are of such interest as to warrant a critical comparison and discussion In order to compare the data of Purvis with the data of Baly, some basis for comparison must be selected. A basis of comparison presents itself in the series of integral numbers of absorption transitions which are functions of the frequencies of the several absorption bands of chlorobenzene This series of numbers for chlorobenzene (in alcoholic solution) may be determined by employing the system of rectangular co-ordinates according to the principles and method previously described in the study of the absorption spectrum and dynamic formulæ of benzene

First, the application will be made to Baly's data on the absorption spectra of chlorobenzene in alcoholic solution In the following Fig 3, the frequencies are indicated on the Y-axis and the absorption transitions on the X-axis According to the present hypothesis the entire 24 absorption transitions function as the origin of the band of highest frequency, namely, 4072, hence the point (4072, 24) Now there can be found passing through this point *only one straight line* which will intersect the abscissæ from the frequency values (Y-axis) at points which have corresponding values on the X-axis (absorption transitions) *approximately equal to whole numbers* This straight line passes through the points (4072, 24) and (3682, 8) involving the bands of highest and lowest frequencies respectively, and the series of whole numbers of absorption transitions which are the linear functions of the frequencies of the seven bands of chlorobenzene are thus found to be 8, 12, 14, 16, 18, 20, 24 The line which relates these numbers with the corresponding frequencies is an approximately straight line. It is important to note that according to the present hypothesis this line should be absolutely straight provided that the data for the oscillation frequencies as determined by Baly are absolutely correct. Be this as it may, the deviations from the straight line are so slight that the series of whole numbers thus ascertained will here be provisionally accepted and employed for purposes of comparison in their relation to Baly's data for chlorobenzene in alcoholic solution On the other hand, if the values for the oscillation frequencies as determined by Purvis be as nearly correct as the data of Baly, they should be related likewise to the same series of whole numbers of absorption transitions Therefore, an

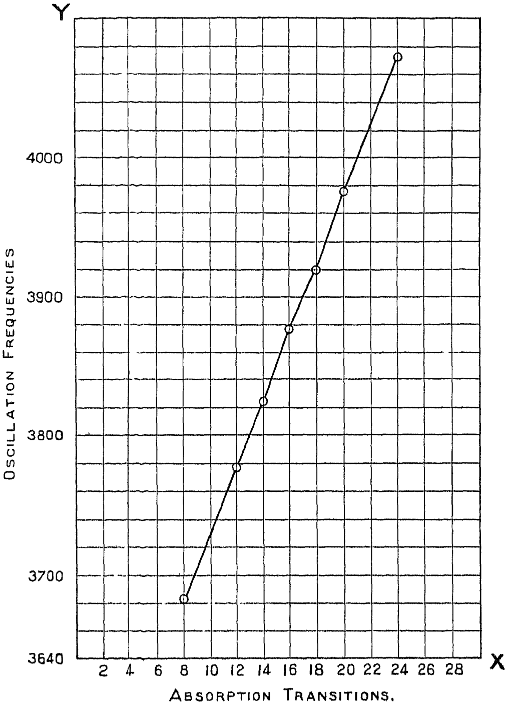


FIG. 3 —Chlorobenzene in Alcohol (Baly)

application of the hypothesis to the data of Purvis naturally follows

In the following Fig. 4 the frequencies of the absorption bands of chlorobenzene in alcoholic solution as determined by

Purvis are indicated on the Y-axis, the absorption transitions, on the X-axis Band Seven of highest frequency, 4082, involving 24 absorption transitions, establishes the point (4082, 24)

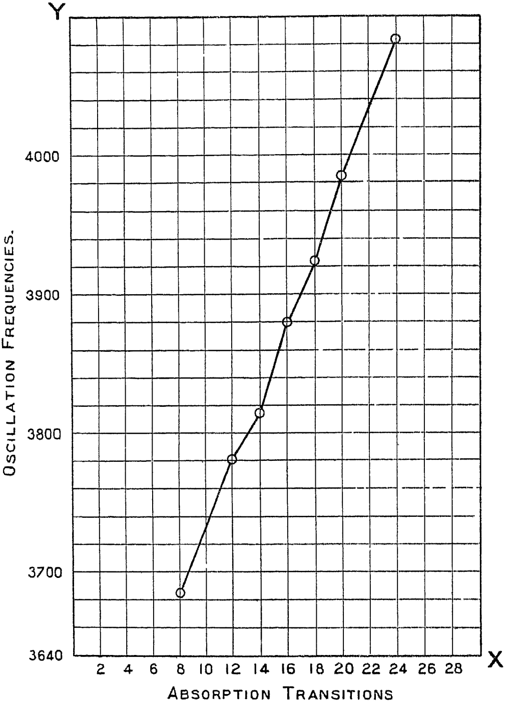


FIG 4—Chlorobenzene in Alcohol (Purvis)

Now, in this instance there cannot be found any straight line passing through this point which will intersect the abscissæ from the frequency values (Y-axis) at points which have corresponding values on the X-axis (absorption transitions) approximately equal to whole numbers Furthermore, if the series of whole numbers related to Baly's data be applied to the data of Purvis, the line which relates these whole numbers with the corresponding frequencies is not a straight line (see Fig 4) Therefore, in terms of the present hypothesis, the values for the frequencies of the absorption bands of chlorobenzene in alcoholic solution as determined by Purvis are not as accurate as the corresponding values determined by Baly. Further evidence of the partial inaccuracy of the data of Purvis on chlorobenzene becomes evident when his data on bromobenzene in alcoholic solution are compared with Baly's data on chlorobenzene.

B. The Absorption Spectrum of Bromobenzene in Alcoholic Solution.

Again, if reference be made to Table III, it will be observed that there is a remarkably close agreement between the values for the oscillation frequencies of the absorption bands of chlorobenzene as determined by Baly and the corresponding frequencies of the bands of bromobenzene as determined by Purvis This naturally leads to the assumption that the series of whole numbers (8, 12, 14, 16, 18, 20, 24) of absorption transitions which are linear functions of the frequencies of the bands of chlorobenzene are likewise linear functions of the frequencies of the bands of bromobenzene. That such is actually the case is shown by again employing the system of rectangular co-ordinates Fig. 5 shows how closely the series of numbers of absorption transitions (X-axis) lend themselves to the formation of a straight line when plotted with the corresponding frequencies (Y-axis) of the bands of bromobenzene. The data of Purvis are employed in Fig 5 In other words, the present hypothesis shows that the frequencies of the absorption bands of chlorobenzene, as determined by Baly, and also those of bromobenzene as determined by Purvis, are linear functions of the same series of numbers of absorption transitions. This is not quite the case with the frequencies of the bands of chlorobenzene as determined by Purvis and discussed in the preceding Section A. Therefore, they cannot be as commensurately exact as the corresponding determinations of Baly. A more definite, in fact, a rigid mathematical comparison of all of the data under consideration will be presented as soon as the values for the oscillation frequencies of the absorption bands of chlorobenzene and bromobenzene in

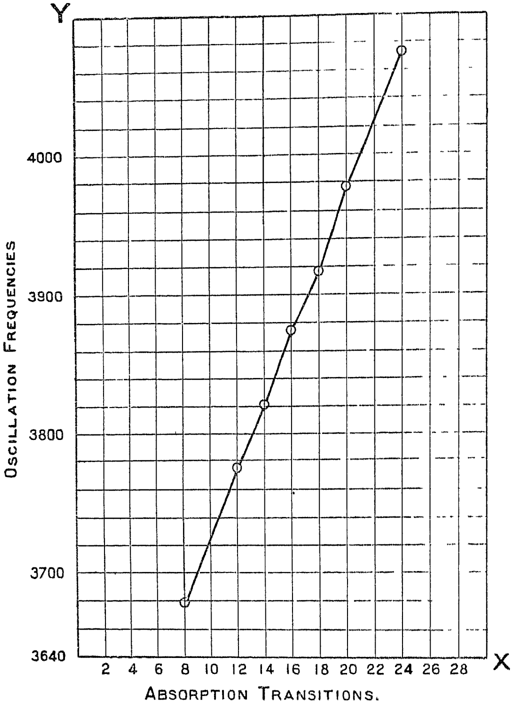


Fig 5 —Bromobenzene in Alcohol (Purvis)

thin films have been considered. All of the data under consideration will then be subjected to an application of the method of least squares.

C. Absorption Spectra of Chlorobenzene and Bromobenzene in Thin Films.

Purvis has found that very thin films of these two substances exhibit seven wide diffuse bands which are comparable in appearance and resemble the solution bands, but they are shifted more towards the less refrangible regions. The bands of the bromobenzene films are shifted more towards the less refrangible region than those of the chlorobenzene films. The frequencies of the bands of these compounds and their respective successive differences are presented in the following Table IV.

TABLE IV

No. of Band	C_6H_5Cl (Thin Films)	Difference.	C_6H_5Br (Thin Films)	Difference
One	3671		3670	
		98		98
Two	3772		3768	
		46		47
Three	3818		3815	
		53		53
Four .	3871		3868	
		41		41
Five	3912		3909	
		62		62
Six .	3974		3971	
		80		78
Seven .	4051		4049	

The columns of differences clearly show that the relative positions of the heads of the bands of each of these compounds are identical. Accordingly, the frequencies of the bands of chlorobenzene and of bromobenzene in thin films likewise should be related to the same series of numbers of absorption transitions. This series, however, cannot be the same as that for the bands of chlorobenzene and bromobenzene in alcoholic solution because the relative positions of bands Six and Seven of the compounds in alcoholic solution are quite different from the relative positions of the same bands of these compounds in thin films. The maximum difference between the sixth and seventh bands in the former case is 98; in the latter case, 80.

The series of numbers of absorption transitions which are linear functions of the frequencies of the bands of chlorobenzene and of bromobenzene when in thin films may be determined according to the method previously described for these compounds when in alcoholic solution In the following Fig 6 the frequencies of the bands of chlorobenzene are indicated on

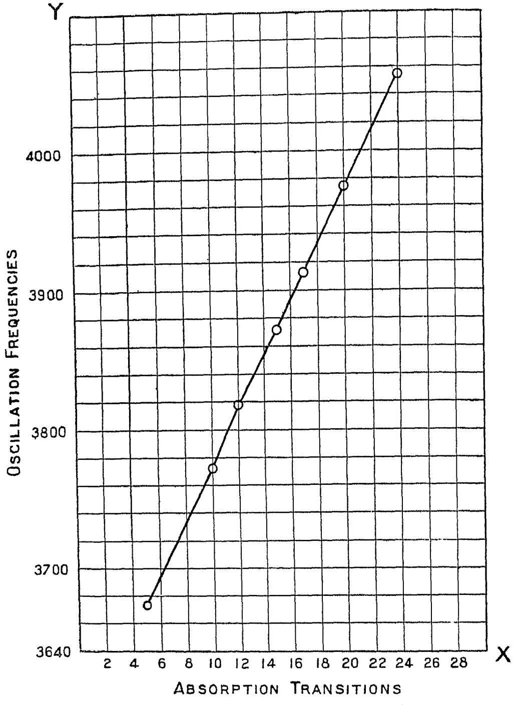


Fig 6 —Chlorobenzene in Thin Films (Purvis)

the Y-axis; the absorption transitions, on the X-axis. Band Seven, frequency 4054, involving 24 transitions, establishes the point (4054, 24) through which only one straight line may be found to pass which will intersect the abscissæ from the frequency values (Y-axis) at points which have corresponding values on the X-axis (absorption transitions) equal to whole numbers. This line establishes the series of transitions (5, 10, 12, 15, 17, 20, 24) which are functions of the frequencies of the corresponding bands (One to Seven) of chlorobenzene in thin films. The same series of whole numbers also functions for the frequencies of the bands of bromobenzene in thin films because the relative positions of the heads of the bands of chlorobenzene and bromobenzene are identical.

D. Application of the Method of Least Squares to Absorption Data.

A more rigid mathematical comparison of all of the data under consideration in this paper is herewith presented in the following Tables V. to IX. inclusive.

TABLE V

CHLOROBENZENE (in alcohol) $y = 24{\cdot}4166x + 3484{\cdot}905$

A.	B (Baly)	C	D
8	3682	3680·237	+ 1·763
12	3777	3777·904	− 0·904
14	3825	3826·737	− 1·737
16	3878	3875·570	+ 2·430
18	3920	3924·403	− 4·403
20	3975	3973·237	+ 1·763
24	4072	4070·903	+ 1·097

TABLE VI.

CHLOROBENZENE (in alcohol). $y = 24{\cdot}9806x + 3478{\cdot}738$

A	B (Purvis)	C	D
8	3685	3678·583	+ 6·417
12	3781	3778·505	+ 2·495
14	3814	3828·466	− 14·466
16	3880	3878·428	+ 1·572
18	3923	3928·389	− 5·389
20	3984	3978·350	+ 5·650
24	4082	4078·272	+ 3·728

TABLE VII.

BROMOBENZENE (in alcohol) $y = 24{\cdot}6904x + 3478{\cdot}524$

A	B (Purvis)	C	D
8	3679	3676·047	+ 2·953
12	3775	3774·809	+ 0·191
14	3821	3824·189	− 3·189
16	3874	3873·570	+ 0·430
18	3917	3922·951	− 5·951
20	3976	3972·332	+ 3·668
24	4073	4071·093	+ 1·907

TABLE VIII

CHLOROBENZENE (in thin films) $y = 19{\cdot}9717x + 3573{\cdot}986$

A	B (Purvis)	C	D
5	3674	3673·844	+ 0·156
10	3772	3773·705	− 1·705
12	3818	3813·646	+ 4·354
15	3871	3873·561	− 2·561
17	3912	3913·505	− 1·505
20	3974	3973·420	+ 0·580
24	4054	4053·307	+ 0·693

TABLE IX

BROMOBENZENE (in thin films) $y = 19{\cdot}9548x + 3570{\cdot}665$

A	B (Purvis)	C	D
5	3670	3670·439	− 0·439
10	3768	3770·213	− 2·213
12	3815	3810·122	+ 4·878
15	3868	3869·987	− 1·987
17	3909	3909·896	− 0·896
20	3971	3969·761	+ 1·239
24	4049	4049·580	− 0·580

In each of the above Tables (V-IX), column A contains the theoretically determined series of whole numbers of absorption transitions which function as the origin of the corresponding oscillation frequencies respectively indicated in column B. The equation for the straight line for each table of data expresses the relationship between the number of absorption transitions (x) and the corresponding oscillation frequency (y). In each case the equation was derived by applying the *method of least squares* to the theoretically determined numbers of absorption transitions (t) in column A, and the experimentally determined frequencies (ν) in column B. By means of these equations, values for the oscillation frequencies have been calculated and are indicated in column C. The deviations of the calculated from the experimentally determined frequencies (i.e., B-C) are recorded in column D.

It will be observed that, with a few exceptions, the deviations show a remarkably close agreement between the calculated and the observed frequencies. Furthermore, a critical test, both of the validity of the rule that the frequencies are linear functions of the numbers of absorption transitions, and of the accuracy of the data in question, may be found by calculating the values for the *probable error* by means of the application of *Peters' formula* for each of the columns of deviations in the above Tables V.-IX. Of course, it is understood that the term "probable error" does not mean that said error is more probable than any other. It signifies that in any subsequent observations the probability of committing an error greater than the probable error is equal to the probability of committing an error less than the probable error. Therefore, the determination of the probable error for each of the above tables of data will give a numerical value which will represent the relative degree of accuracy of the several sets of data in the above tables, and also serve as a test of the validity of the rule. The following tabulation comprises the results of the application of Peters' formula for the probable error of a single observation :—

$r = 0{\cdot}8453 \dfrac{\Sigma v}{\sqrt{n(n-1)}}$, Σv = sum of the deviations for each set of data ; n = number of measurements of frequencies, namely 7, in each table of data.

Tables		Σv	r
V.	Chlorobenzene in alcohol (Baly) . .	14·0970	1·838
VI.	" " " (Purvis) . .	39·7169	5·179
VII.	Bromobenzene " " (") .	18·2891	2·385
VIII.	Chlorobenzene " thin films (") . .	11·5537	1·507
IX.	Bromobenzene " " " (") . .	12·2316	1·595

A comparison of the values in the above table shows that the probable error of a single observation for each table of data (with the exception of VI and possibly VII, i e, chlorobenzene and bromobenzene in alcohol according to Purvis), is practically within the limits of error of experimental observation

The developments presented in this chapter warrant the following conclusions —

(1) The oscillation frequencies of the absorption bands of chlorobenzene and of bromobenzene, either in alcoholic solution or in thin films, are linear functions of a corresponding series of whole numbers In terms of the present hypothesis, the whole number which is related to a given frequency represents the number of absorption transitions which function as the origin of the band of given frequency.

(2) One series of numbers of absorption transitions applies equally to the data for chlorobenzene (Baly) and bromobenzene (Purvis) when observations were made of the compounds in alcoholic solution

(3) Another series of numbers of absorption transitions applies equally to the data of Purvis for chlorobenzene and for bromobenzene when observations were made of the pure substances in thin films

(4) The probable errors for the observations of the substances in thin films are not only more nearly equal but they are also smaller than the corresponding probable errors for the observations of the substances in alcoholic solution.

(5) The possibility of representing the frequencies of the absorption bands of a compound as linear functions of a series of whole numbers affords a means of determining the relative accuracy of the observations For example, the data of Purvis for chlorobenzene in alcoholic solution (Table VI) do not conform to this condition as is evident in Fig 4 Furthermore, the probable error for this set of observations is not commensurate with the probable errors for the other tables of data, and therefore indicates greater errors in the determinations of the frequencies of the absorption bands of chlorobenzene than in the other data under discussion

E. The Origin of the Absorption Bands.

There now remains for consideration the possibility of relating each of the seven absorption bands of chlorobenzene and bromobenzene to its probable source In other words, in terms of the present hypothesis each absorption band owes its origin to the existence of certain numbers and groups of absorption transitions. The groups of absorption transitions which are common to benzene, chlorobenzene, and bromobenzene have been indicated in Table II. The principles employed in relating the seven bands of benzene to their respective groups of absorption transitions have been described in Chapter XVIII., Section E. They are applied, herewith, in the same manner to the absorption bands, of chlorobenzene and bromobenzene.

Two different series of numbers of absorption transitions have been indicated in this chapter, namely, the series (8, 12, 14, 16, 18, 20, 24) for either chlorobenzene or bromobenzene in alcoholic solution; and the series (5, 10, 12, 15, 17, 20, 24) for either chlorobenzene or bromobenzene in thin films. Accordingly, the two different schemes presented in the following Tables X and XI embody the possible arrangements of the several groups of absorption transitions which may function as

TABLE X

CHLOROBENZENE AND BROMOBENZENE IN ALCOHOLIC SOLUTION

Band	Origin	Number of Absorption Transitions
One	$IV_2 + \alpha_2 + \beta_1 + \gamma_1 + \delta_2$ . . .	8
Two	$IV_2 + \alpha_2 + \beta_1 + \gamma_1 + \delta_2 + (I_4 \text{ or } VII_4)$ . .	12
Three	$IV_2 + \alpha_2 + \beta_1 + \gamma_1 + \delta_2 + (I_4 \text{ or } VII_4) + (II_2 \text{ or } VI_2)$.	14
Four	$IV_2 + \alpha_2 + \beta_1 + \gamma_1 + \delta_2 + (I_4 \text{ or } VII_4) + (II_2 \text{ or } VI_2) + (III_2 \text{ or } V_2)$	16
Five	$IV_2 + \alpha_2 + \beta_1 + \gamma_1 + \delta_2 + (I_4 \text{ or } VII_4) + (II_2 \text{ or } VI_2) + III_2 + V_2$	18
Six	$IV_2 + \alpha_2 + \beta_1 + \gamma_1 + \delta_2 + (I_4 \text{ or } VII_4) + II_2 + VI_2 + III_2 + V_2$.	20
Seven	$IV_2 + \alpha_2 + \beta_1 + \gamma_1 + \delta_2 + I_4 + VII_4 + II_2 + VI_2 + III_2 + V_2$ . .	24

TABLE XI.

CHLOROBENZENE AND BROMOBENZENE IN THIN FILMS.

Band.	Origin	Number of Absorption Transitions.
One	$IV_2 + \{(\alpha_2 + \beta_1) \text{ or } (\gamma_1 + \delta_2)\}$	5
Two	$IV_2 + \{(\alpha_2 + \beta_1) \text{ or } (\gamma_1 + \delta_2)\} + (\beta_1 \text{ or } \gamma_1) + (I_4 \text{ or } VII_4)$ . . .	10
Three	$IV_2 + \{(\alpha_2 + \beta_1) \text{ or } (\gamma_1 + \delta_2)\} + (\beta_1 \text{ or } \gamma_1) + (I_4 \text{ or } VII_4) + (II_2 \text{ or } VI_2)$	12
Four	$IV_2 + \alpha_2 + \delta_2 + (\beta_1 \text{ or } \gamma_1) + (I_4 \text{ or } VII_4) + (II_2 \text{ or } VI_2) + (III_2 \text{ or } V_2)$	15
Five	$IV_2 + \alpha_2 + \delta_2 + (\beta_1 \text{ or } \gamma_1) + (I_4 \text{ or } VII_4) + (II_2 \text{ or } VI_2) + III_2 + V_2$.	17
Six	$IV_2 + \alpha_2 + \delta_2 + \beta_1 + \gamma_1 + (I_4 \text{ or } VII_4) + II_2 + VI_2 + III_2 + V_2$.	20
Seven	$IV_2 + \alpha_2 + \delta_2 + \beta_1 + \gamma_1 + I_4 + VII_4 + II_2 + VI_2 + III_2 + V_2$ . .	24

the origin of the corresponding absorption bands The notation is the same as that previously employed For example, the symbol IV_2 represents the two absorption transitions of group IV, namely, $C' \rightleftharpoons C \rightleftharpoons D \rightleftharpoons D'$ and $C'' \rightleftharpoons C \rightleftharpoons D \rightleftharpoons D''$

In comparing the above schemes it will be observed that the absorption transitions of group IV. involve the centric electromers C and D (see Fig I, p. 188) which constitute the nucleus, so to speak, of the complete system of dynamic equilibria of the electromers of benzene, chlorobenzene, and bromobenzene The other groups of transitions are successively and collectively embraced, producing in a natural sequence the series of seven whole numbers which are linear functions of the oscillation frequencies of the seven bands, and which may probably represent the number of the specifically indicated absorption transitions involved in the production of the corresponding absorption band

It has also been noted that the series of numbers of transitions related to the absorption bands of chlorobenzene and bromobenzene in alcoholic solution is not identical with the series of numbers of transitions related to the absorption bands of these compounds in thin films The explanation of this difference may be found in the fact that in alcoholic solution the molecules of the dissolved compound cannot be as closely compacted as they are in thin films of the pure substance Consequently, the relative positions of the electromers of the compound are different and this in turn may lead to different arrangements of the various groups of the electromers so that one series of groups of transitions would function as the origins of the bands of the compound in solution while another series of groups of absorption transitions would determine the origins of the bands of the compound in the pure state, that is, in thin films.

F. The Non-Selective Absorption of Iodobenzene.

The absorption spectra of solutions of iodobenzene have been investigated by Pauer[129] who found no bands. Purvis[130] also studied the absorption spectra of various concentrations of alcoholic solutions of iodobenzene, and of thin films of the pure substance No bands were found in either case, whereas each of the corresponding mono-substituted derivatives of benzene, chlorobenzene and bromobenzene, exhibited seven bands. This anomalous behaviour on the part of iodobenzene demands an explanation.

Purvis has offered the explanation that "the heavy iodine atom is the controlling force, and it damps and dislocates the movements of the atoms of the benzene nucleus as well as the alkyl side chains, so that the rythmical oscillations or vibrations are destroyed, and no selective absorption is possible". It is undoubtedly true that the mass, the intrinsic characteristics, the orientation of the atoms of the benzene nucleus and its substituents, and the physical conditions of the vibrating system, may all function in determining the nature of the absorption spectra, but the absorption hypothesis of Purvis and his explanation of the non-selective absorption of iodobenzene and its derivatives must be regarded as deficient for the following reasons:—

(1) Purvis fails to define the nature or type of the rhythmical oscillations or vibrations of the so-called "oscillation centres".[131]

(2) The assumption that the weight of the iodine atom in iodobenzene damps and dislocates the movements of the atoms of the benzene nucleus, thereby preventing selective absorption, is somewhat arbitrary in that it fails to take into consideration another equally probable condition, namely, that the weights of other atoms, chlorine and bromine, which replace one hydrogen atom of benzene likewise may damp, or at least dislocate, the movements of the atoms of the benzene nucleus and, thereby, either alter or prevent selective absorption. This, however, is not the case since chlorobenzene and bromobenzene each show seven absorption bands—*the same number exhibited by benzene.* An inspection of the following tabulation further emphasizes the significance of this criticism:—

A	B	C
$C_6H_5 . H$	H = 1·008	—
$C_6H_5 . Cl$	Cl = 35·46	35·46 ÷ 1·008 = 35·17
$C_6H_5 . Br$	Br = 79·92	79·92 ÷ 35·46 = 2·25
$C_6H_5 . I$	I = 126·92	126·92 ÷ 79·92 = 1·58

Column A contains the formulæ of the compounds under consideration. Column B indicates the atomic weights of the substituents which replace one hydrogen atom of benzene; benzene, in turn, being regarded as phenyl hydride, a mono-substituted derivative. Column C embodies data showing that the chlorine atom which replaces one hydrogen atom is 35 17 times as heavy as the replaced hydrogen atom of benzene Notwithstanding this very great difference in the ratio of the weights of the substituents chlorine and hydrogen, chlorobenzene shows the same number of absorption bands as does phenyl hydride or benzene Furthermore, the bromine atom which may be regarded as replacing the chlorine atom is 2 25 times as heavy as the displaced chlorine atom, nevertheless, the resulting compound, bromobenzene, shows seven absorption bands Finally, the iodine atom replacing the bromine atom is only 1·58 times as heavy as the displaced bromine atom, but iodobenzene shows no absorption bands Therefore, in view of these decreasing ratios of the weights of the substituents, hydrogen, chlorine, bromine, and iodine, to one another, the non-selective absorption of iodobenzene should not be attributed to the weight of the iodine atom How then is the non-selective absorption of iodobenzene to be explained?

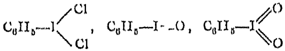
The present hypothesis has explained selective absorption by the occurrence of definitely described rearrangements of valencies within the electronic formulæ of the compound in dynamic equilibria These rearrangements, contraplex-diplex transitions or absorption transitions, must be interfered with in some definite way if the selective absorption of the compound is to be prevented Therefore, if chlorobenzene and bromobenzene each shows seven absorption bands and iodobenzene shows none, it must be concluded that the chlorine and bromine atoms in chlorobenzene and bromobenzene do not prevent the occurrence of absorption transitions, but that the iodine atom in iodobenzene (or its derivatives) inhibits, in some manner, the occurrence of absorption transitions. Now the existence of absorption transitions has been shown to depend upon rearrangements of the centric valences of the nucleus. Accordingly, *the non-selective absorption of iodobenzene must be due to the inhibition or prevention of the centric rearrangements of the benzene nuclei by the substituted iodine atom*

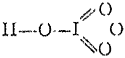
Why does not the substituted chlorine and bromine atom in chlorobenzene and bromobenzene inhibit centric rearrangements and thereby prevent the occurrence of the absorption transitions and the consequent selective absorption of these compounds? The answer to this question may be found in the particular chemical nature of the substituents chlorine, bromine, and iodine In chlorobenzene and bromobenzene the substituents are completely saturated, i e , they form no addition compounds through the intermediate agency of the chlorine or bromine atoms On the other hand, the iodine atom in iodobenzene is unsaturated since it combines directly with chlorine to form iodobenzene dichloride according to the equation,[132]

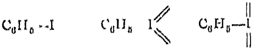
$$C_6H_5I + Cl_2 \rightarrow C_6H_5ICl_2.$$

The existence of the compounds, iodosobenzene, C_6H_5IO, and iodoxybenzene, $C_6H_5IO_2$, affords additional evidence of the unsaturated condition of the iodine atom in iodobenzene The corresponding derivatives of chlorobenzene and bromobenzene are unknown.

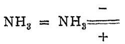
The manner in which the unsaturated iodine atom inhibits the centric rearrangements of the benzene nucleus may be made evident by considering first the structural formulæ of the compounds iodobenzene dichloride, iodosobenzene, and iodoxybenzene, namely,



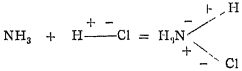
In iodobenzene, iodine is univalent; in iodobenzene dichloride and iodosobenzene, tervalent ; in iodoxybenzene, quinquevalent. In periodic acid, HIO_4, structurally represented  O, the maximum valence of iodine is seven. Hence it may be concluded that the unsaturated iodine atom in iodobenzene may possess two, four, and possibly six free or potential valences which may be represented as follows:—



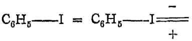
This property of certain atoms to display a capacity for increasing their degree of saturation is well known, and generally the additional valences manifest themselves, or are called into play, so to speak, in pairs. Furthermore, the two valences of such a pair are of opposite sign or polarity. For instance, in the reaction, $NH_3 + HCl \rightarrow NH_4Cl$, the nitrogen atom changes its valence from three to five, that is, the valence is increased by two In terms of the electronic conception of positive and negative valences this reaction is represented as follows —



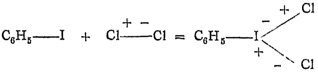
$$NH_3 = NH_3\overset{-}{\underset{+}{=}}$$



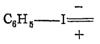
Analogously the iodine atom in iodobenzene increases its valence by two when combining with chlorine, thus —

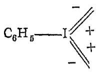


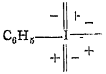
$$C_6H_5—I = C_6H_5—I\overset{-}{\underset{+}{=}}$$



Analogously the several possible degrees of saturation of the iodine atom in iodobenzene may be represented as follows, the additional valences appearing in pairs —

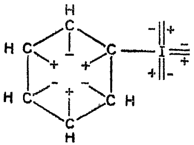




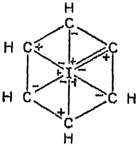


In the last formula the iodine atom displays its maximum valence of seven One valence unites the atom to the benzene ring, and each of the three pairs of latent or potential valences comprises one positive and one negative valence

Of the six centric valences of the benzene nucleus, three are positive and three are negative Hence, the centric valences may be regarded as consisting of three pairs of free or potential valences, each pair consisting of one positive and one negative valence Therefore, all of the free or potential valences of iodobenzene may be indicated in the following structural formula —



Now the unsaturated valences of the iodine atom and the centric valences of the benzene nucleus would most naturally engage or neutralize one another as may be indicated in the following formula in which the substituted iodine atom has been placed in the centre for the sake of symmetry :—



This electronic formula definitely illustrates how the centric valences of the benzene nucleus may be either "bound" or interfered with by the unsaturated valences of the substituted iodine atom. Therefore, the non-selective absorption of iodobenzene naturally may be attributed to the unsaturated state of the iodine atom, the free or potential valences of which bind or interfere with the centric valences of the benzene nucleus, thereby inhibiting centric rearrangements, and consequently preventing the occurrence of absorption transitions.

CHAPTER XX.

DYNAMIC ELECTRONIC FORMULÆ AND THE ULTRAVIOLET ABSORPTION SPECTRUM OF NAPHTHALENE

THE electronic conception of valence and the absorption-transition hypothesis have been applied, respectively, to the constitution and to the ultraviolet absorption spectra of benzene, chlorobenzene, and bromobenzene They are extended, herewith, to the constitution and ultraviolet absorption spectrum of naphthalene.

A. Electronic Formulæ of Naphthalene.

Benzene nuclei of the centric type were composed of the five electronic types of carbon atom (see p 49) Each nucleus embraced three pairs of the combined types I. and V , II. and IV , or III and III , symmetrically co-ordinated. Only six centric electronic formulæ, centric electromers of benzene, were possible. By extending this method of building up electronic formulæ to the constituent atoms of the naphthalene molecule, two and only two, perfectly symmetrical centric electromers are possible, namely, A and B of Fig 7 —

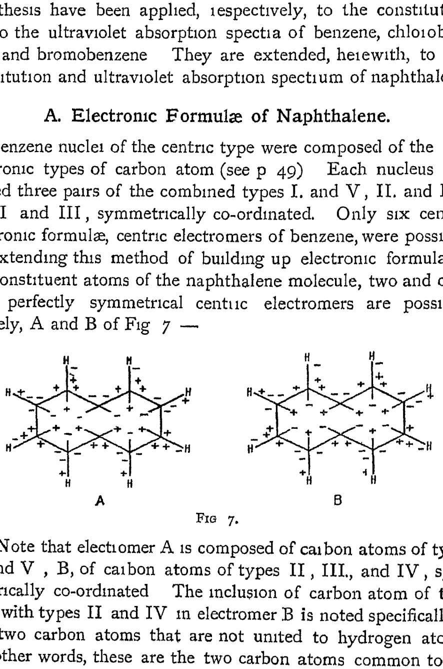


FIG 7.

Note that electromer A is composed of carbon atoms of types I and V , B, of carbon atoms of types II , III., and IV , symmetrically co-ordinated The inclusion of carbon atom of type III with types II and IV in electromer B is noted specifically in the two carbon atoms that are not united to hydrogen atoms. In other words, these are the two carbon atoms common to the two benzene rings which constitute the naphthalene molecule It is very significant that the hydrogen atoms in positions 1, 3, 6, and 8 of the naphthalene ring are negative while those in positions 2, 4, 5, and 7 are positive.

It is quite possible to interpret many of the chemical properties and reactions of naphthalene in terms of the polarities of these hydrogen atoms of the electronic formula of naphthalene, somewhat as substitution in the benzene nucleus, and many chemical properties of benzene and its derivatives were interpreted fully in terms of the electronic formula of benzene. This monograph has limited its interpretation of chemical reactions chiefly to benzene and its derivatives The electronic formulæ of condensed benzene nuclei, such as naphthalene, anthracene, and phenanthrene, are dealt with in relation to phenomena of light absorption and fluorescence.

B. Systems of Dynamic Equilibria of the Electromers of Naphthalene.

A complete scheme of the systems of dynamic equilibria of the electromers of naphthalene is given in Fig. 8 (p 226). The polarities of the valences which engage the hydrogen atoms of naphthalene are not indicated because they do not function in the centric rearrangements and related systems of equilibria.

Each electronic formula is to be regarded as the plane projection of a space formula. The centric electromer A is the intermediate phase between the three possible phasotropic electromers A′, A″, and A‴. By means of centric rearrangement, A, composed of carbon atoms of the types I. and V., may be converted into B, composed of carbon atoms of the types II., III, and IV. In turn, B functions as the intermediate phase between the phasotropic electromers B′, B″, and B‴. This scheme presents six primary and nine secondary systems of phasotropic equilibria. Two of the primary and the nine secondary systems involve contraplex-diplex transitions which are assumed to constitute both the structural and the electronic explanation of the ultraviolet absorption spectrum of naphthalene.

Before tabulating and discussing the several systems of contraplex-diplex transitions, i.e., absorption transitions, it will be necessary to review briefly the relation between the absorption spectrum of naphthalene and its chemical constitution as conceived by Baly and Tuck[133]

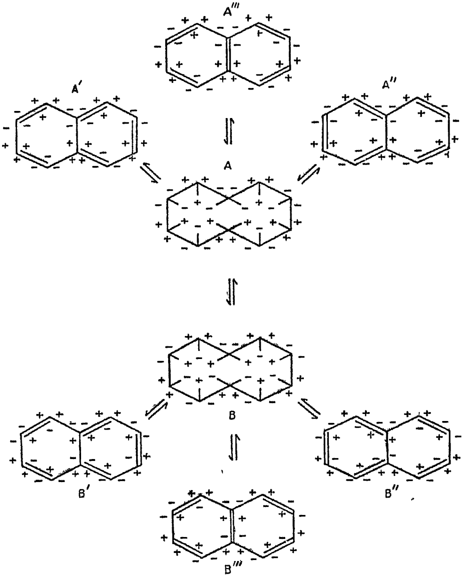
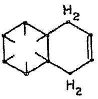


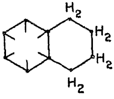
FIG 8.

C. The Absorption Spectrum of Naphthalene.

Baly and Tuck state that "there are three absorption bands, namely, two narrow ones at $1/\lambda = 3125$ and 3220 respectively, and a broad band with its head at about $1/\lambda = 3700$" In attempting to correlate the position of these bands with the constitution of naphthalene Baly and Tuck maintain that "from the ease with which naphthalene is reduced in hot alcoholic solution by metallic sodium to the dihydro compound (I.),



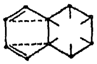
I



II

and the further reduction to the tetrahydro compound (II), this being the final product of the reduction, there is little doubt that one of the rings is truly benzenoid, and the other contains two ethylenic double bonds, which according to Thiele's law, give their maximum effect at the two extremes, that is to say, at positions 1 and 4". Baly and Tuck then conclude that "Naphthalene therefore would seem to consist of two rings, of which one is truly benzenoid, and the other contains two conjugated double linkings. There is no reason to insist that the two rings are permanently endowed with one of the two above characters, in fact it seems that the interchange of these characters between the rings is perfectly possible, and no doubt is continually taking place."

In seeking the origin of the three absorption bands in the spectrum of naphthalene, Baly and Tuck insist that the broad absorption band with its head at $1/\lambda = 3700$ is due to the benzenoid motions of the naphthalene molecule and attribute this band to that half of the molecule which is benzenoid in character. On the other hand, they maintain that the two narrow bands at $1/\lambda = 3125$ and 3220, which are nearer to the red end of the spectrum than any of the benzene bands, must be due to the isorropesis between the benzenoid tautomerism of the ring and the ethylenic double linkings of the other half of the molecule. Hence naphthalene is represented by the formula—

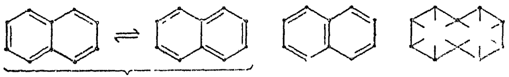


in which isorropesis between atoms 2 and 3 with the benzenoid system is indicated by the dotted lines.

The foregoing suppositions of Baly and Tuck are open to the following three possible objections:—

(1) Since the naphthalene molecule is generally conceded to

be symmetrically constituted and to conform structurally to either of the three following symmetrical types —



it naturally follows that any systems of vibrations of the naphthalene molecule should likewise be symmetrically developed and involve only symmetrical configurations

(2) The fact that certain derivatives of naphthalene (such as the previously noted dihydro- and tetrahydro-naphthalenes) seem to consist of two rings, one of which is truly benzenoid while the other contains two conjugated double linkings, cannot be accepted as proof that naphthalene itself consists of two kinds of rings Baly and Tuck partially admit this objection in their statement that "there is no reason to insist that the two rings are permanently endowed with one of the two above characters; in fact, it seems that the interchange of these characters between the rings is perfectly possible, and no doubt is continually taking place". This admission is incompatible with their fundamental assumption that one ring of the naphthalene molecule is benzenoid and that its vibrations produce band $1/\lambda = 3700$, while on the other hand the ethylenic ring permits of isorropesis between the atoms 2 and 3 with the benzenoid system, thereby accounting for bands $1/\lambda = 3125$ and 3220.

(3) The hypotheses of Baly and others fail to indicate the existence of any quantitative relationship between the actual oscillation frequencies of the absorption bands and their proposed dynamic formulæ

In the proposed electronic formulæ for naphthalene and in the systems of dynamic equilibria of the various electromers there is perfect symmetry both in the structure of the electromers and in the transitions they undergo. Moreover, it is possible to show that a quantitative relationship in the nature of a linear function exists between the actual oscillation frequencies of the absorption bands of naphthalene and the numbers of absorption transitions which may be specifically indicated in the systems of dynamic equilibria of the various electromers.

D. Correlation of Oscillation Frequencies and Absorption Transitions.

Referring to the complete scheme of dynamic equilibria of the electromers of naphthalene (see Fig 8), observe that there occurs only one centric rearrangement transition, namely, A ⇌ B The phasotropic electromers, A′, A″, and A‴, are each derived from the centric electromer A and each contains five *diplex* double bonds They may therefore be regarded as mutually equivalent in these systems of equilibria in which they are involved On the other hand, B′, B″, and B‴, each derived from the centric electromer B, are not mutually equivalent since B′ and B″ each contain five *contraplex* double bonds while B‴ contains four *contraplex* and one *diplex* double bonds B′ and B″ may therefore be regarded as mutually equivalent while B‴ stands in a class by itself* Thus there are three groups of phasotropic electromers, namely —

A′ =⊃= A″ =⊃= A‴, each containing *five diplex* double bonds ,
B′ =⊃= B″, each containing *five contraplex* double bonds ,
B‴, containing *one diplex* and *four contraplex* double bonds

The primary and secondary systems of phasotropic equilibria are indicated in the following tables Those equilibria involving contraplex-diplex, or absorption, transitions are each followed by an asterisk ·—

Primary Systems

$$\begin{array}{l} A'-A-A'' \\ A'-A-A''' \\ A''-A-A''' \end{array}$$

$$\alpha\left\{\begin{array}{l} B'-B-B'' \\ B'-B-B'''\ * \\ B''-B-B'''\ * \end{array}\right.$$

Secondary Systems

$$\mathrm{I}\left\{\begin{array}{l} A'-A-B-B'''\ * \\ A''-A-B-B'''\ * \\ A'''-A-B-B'''\ * \end{array}\right.$$

$$\mathrm{II}\left\{\begin{array}{l} A'-A-B-B'\ * \\ A''-A-B-B'\ * \\ A'''-A-B-B'\ * \\ A'-A-B-B''\ * \\ A''-A-B-B''\ * \\ A'''-A-B-B''\ * \end{array}\right.$$

Only two of the primary systems (group α) present absorption transitions The nine secondary systems are naturally divided into two groups. Group I. presents three transitions, each of which involves B‴ in dynamic equilibrium with A′, A″, and A‴, respectively. Group II presents six transitions involving B′ and B″ in dynamic equilibria with A′, A″, and A‴, respectively Hence the following summary —

---

* This type of an electromer functions in the production of the fluorescence band Electronic formulæ in relation to fluorescence will be considered in the following chapter.

Group α	2 absorption transitions.
Group I	3 " "
Group II	6 " "

The correlation of the numbers of these transitions with the oscillation frequencies of each of the bands in the ultraviolet absorption spectrum of naphthalene must now be developed The oscillation frequencies of the heads of each of these bands, as determined by Baly and Tuck, are as follows —

Band One	$1/\lambda = 3125$
Band Two	$1/\lambda - 3220$
Band Three	$1/\lambda = 3700$

Now the two transitions of group α and the three transitions of group I. (i e, five transitions), involve the electromer B‴ which differs from each of the other phasotropic electromers of naphthalene These five transitions may be assumed to function in the production of one of the absorption bands, presumably band One of lowest oscillation frequency, 3125 In other words, the vibrations of these five absorption transitions are assumed to be synchronous with light waves of frequency 3125. On the other hand, there remain the six absorption transitions of group II which do not involve the electromer B‴. Hence the vibrations of these six absorption transitions may be synchronous with light waves of frequency 3220, i e, band Two. In other words, the oscillation frequencies 3125 and 3220 have been assumed to be functions of the whole numbers 5 and 6 respectively The problem now demanding solution is the determination of that whole number which is a function of the oscillation frequency 3700 of the remaining band Three How is this number to be derived?

Again, by employing the system of rectangular co-ordinates, it is possible to determine the number of absorption transitions involved in the production of band Three. In Fig. 9, the frequencies are indicated on the Y-axis and the numbers of contraplex-diplex transitions on the X-axis. Five transitions have been assumed to function as the origin of band One of frequency 3125, six transitions as the origin of band Two, frequency 3220 Now if a straight line be extended through the points (3125, 5) and (3220, 6) its extension will intersect the perpendicular from frequency 3700 at a point which has a corresponding value on the X-axis equal to the whole number eleven. In other words, there are eleven absorption transitions functioning as the origin of band Three, frequency 3700. Furthermore, it is remarkable that this number 11, as thus derived, is equal to the sum of 5 plus 6 In terms of the absorption transition hypothesis this numerical result permits of only one conclusion, namely, that the five transitions which function as the origin of band One, and the six transitions which function as the origin of band Two, must function all together as the origin of the broad band Three. In other words, the vibrations of the entire 11 absorption transitions are synchronous with light waves of oscillation frequency 3700

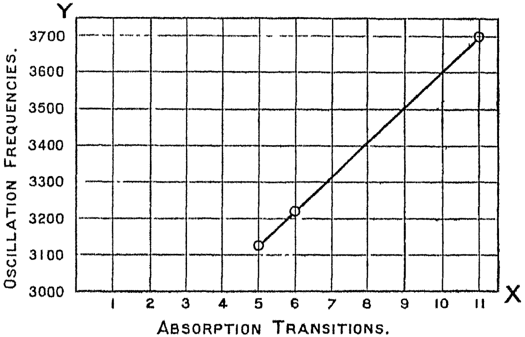


FIG. 9. Naphthalene (Baly and Tuck).

The scheme relating each of the absorption bands of naphthalene to its possible source is presented in tabular form as follows (the nomenclature is identical with that employed in the two preceding chapters) :—

Band.	Origin	Number of Absorption Transitions Involved
3126	$I_1 + \alpha_1$	5
3220	II_6	6
3700	$I_1 + \alpha_1 + II_6$	11

The equation for the straight line which relates the whole numbers, 5, 6, and 11, with the respective frequencies 3125 3220, and 3700, calculated according to the method of least squares, is ($y = 95{\cdot}8871x + 2645{\cdot}1613$)

In the following table, column A contains the theoretically determined whole numbers represented by (x), column B, the experimentally determined oscillation frequencies represented by (y), column C, the frequencies as calculated from the equation $y = 95{\cdot}8871x + 2645{\cdot}1613$ —

A	B	C	D
5	3125	3124·5968	+ 0·4032
6	3220	3220·4839	− 0·4839
11	3700	3699·9194	+ 0·0806

Note that the deviations, in column D, of the calculated from the actual oscillation frequencies are each less than one unit, a quantity exceedingly smaller than any deviation due to possible errors in experimental observation These results further substantiate the hypothesis that the oscillation frequencies of the absorption bands of a given compound are functions of the number of absorption transitions involved in the systems of dynamic equilibria of its electromers

The bearing of these developments upon the question of colour and constitution is at once apparent since a coloured substance is one which exerts strong absorption within the ordinary limits of vision Therefore the proposed absorption transition hypothesis which mathematically relates absorption and constitution should likewise function as the basis of the explanation of colour in relation to constitution

CHAPTER XXI

FLUORESCENCE IN RELATION TO ELECTRONIC FORMULÆ

SINCE it has been possible to interpret the absorption of light in terms of electronic formulæ and absorption transitions, it naturally follows that fluorescence, notably manifested by such compounds as anthracene and phenanthrene, also may be interpreted by means of electronic formulæ and a new type of contraplex-diplex transition termed "*fluorescence transitions*".

Since fluorescence is produced only when the incident rays contain vibrations which the medium is capable of absorbing, it follows that the relation between fluorescence and absorption is to a certain extent reciprocal. Not only can absorption of light cause fluorescence, but fluorescence in many cases, as shown by Burke,[134] increases the intensity of absorption. Hence, it is the purpose of the present chapter to extend the electronic conception of positive and negative valences and of contraplex-diplex transitions (as previously developed and illustrated in relation to absorption spectra in the three preceding chapters) to the interpretation of the phenomena of fluorescence. In other words, the relationship between chemical constitution and fluorescence will be considered from the standpoint of the existence of contraplex-diplex transitions within the systems of dynamic equilibria of the electromers of fluorescent compounds. A comprehension of the proposed fluorescence hypothesis necessitates, in the first place, a brief review of the foremost theories relating to fluorescence and constitution.

A. Fluorescence Theories in Relation to the Electronic Fluorescence Hypothesis.

A survey of fluorescent compounds by Rich. Meyer[135] led to his "fluorophore" theory which, in its original form, serves as an excellent means of classifying fluorescent compounds, but it affords no explanation of the relation between chemical constitution and fluorescence

As a result of the researches of J Stark[136] on ultraviolet fluorescence, Meyer inverted his former view that the fluorophore is the seat of fluorescence, and both Stark and Meyer,[137] have concluded that in aromatic substances *the benzene nucleus is the carrier of fluorescence,* while the fluorophores and various substituents act so as to bring the fluorescent vibrations within the visible portion of the spectrum The condensation of benzene nuclei accomplishes the same result

The extensive researches of Kauffmann[138] culminating in the luminophore and fluorogen theory also leads to the conclusion that in aromatic compounds the benzene nucleus is the seat of fluorescence, but this is not evoked until two kinds of groups—the auxochrome and fluorogen—have been introduced into certain positions The introduction of the auxochrome excites luminescence, thereby indicating the approaching state of fluorescence The subsequent addition of a luminophore perfects the process in the production of fluorescence

Francesconi and Bargellini[139] also admit the important part played in fluorescence by the benzene nucleus. Recognizing that the observations of Meyer and Kauffmann are concerned chiefly with visible fluorescence, they claim that *all aromatic compounds are fluorescent* and that *it is premature to attempt to explain the action of various substituents.* Nevertheless, they classify substituents according to their action on the fluorescence of the parent substance Those substituents which increase the fluorescence are called "auxoflores," and those which depress it, "bathoflores".

It is important to the development of the electronic fluorescence hypothesis to note that the common point of agreement in each of the above theories is the tendency to relate the origin of fluorescence to the *benzene nucleus.*

The relation between tautomeric change and fluorescence was originally embodied in the theory of Wiedemann,[140] that the molecule of a fluorescent substance exists in two forms, one of which is more stable than the other. The stable form absorbs the energy of light vibration, and is thereby transformed into the less stable modification which spontaneously passes back to the stable form, emitting the previously absorbed energy as the fluorescent light Wiedemann maintained that the two varieties of substance may be produced by the shifting of an atom within the molecule, and that the fluorescent light is directly due to the vibrations in the ether which are set up by the motions of this atom.

Hewitt's theory[111] of double symmetric tautomerism involves the conception of Wiedemann that a fluorescent substance must exist in interchangeable forms. For instance, anthracene (Fig. 10), and di-phenylpyrone-sulphate (Fig 11) present the following changes:—

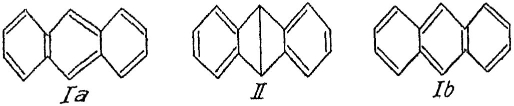


Fig. 10.

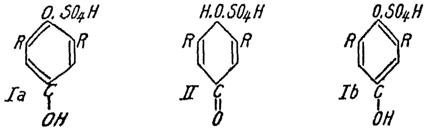


Fig. 11.

In either of the above figures the molecule (I*a*) passes to (II), and then to (I*b*), whereupon the process is repeated in the reverse direction. The molecules (I*a*) and (I*b*) are chemically identical. Hewitt likens these changes to the movements of a swinging pendulum. The limiting positions in the amplitude of vibration correspond to forms (I*a*) and (I*b*) while the position of rest, so to speak, is represented by form (II).

It should here be noted that the changes from one form to another are accomplished in two distinct ways: (1) In anthracene the changes are due solely to a *rearrangement of the positions of the double bonds*, i.e., to changes in the direction of valences. (2) In di-phenylpyrone-sulphate, the rearrangement of double bonds is accompanied by a change in the position of a hydrogen atom. The significance of these changes from an electronic standpoint will appear in the definition of the term "fluorescence transition," which will be developed in a subsequent paragraph.

Let it now be recalled that Wiedemann maintained that fluorescence was due to vibrations set up by the motion or the wandering of an atom, but Drude[112] has shown that the vibrations of the atom itself, or the group of positive electrons must correspond to the infra-red portion of the spectrum, while the periods in the visible and ultraviolet region are due to dispersional or valency electrons Therefore, the second form of the substance required by Wiedemann's theory need not be produced by the movement of an atom, but merely by *the change in position of an electron or valency* Since any change in the position of an atom is accompanied by a change in the positions of the double bonds, it follows that Hewitt's examples of double symmetric tautomerism given above will fulfil either one or both of these conditions

From this brief review of the foremost fluorescence theories, the following conclusions may be drawn.—

(1) The origin of fluorescence in aromatic compounds is related in some way to the benzene nucleus

(2) Physico-chemical evidence shows that the affinities of the benzene nucleus are in a state of continual oscillation

(3) Physical theories require the presence of mobile negative electrons or valencies in the molecules of fluorescent compounds

Therefore, any hypothesis which may be designed to express the relationship between chemical constitution and fluorescence must correlate these three conclusions

B. Fluorescence Transitions.

In the preceding chapters it has been shown that absorption of light is due to the existence of contraplex-diplex transitions within the systems of phasotropic equilibria of the various electromers of a given compound *These electronic systems of phasotropic equilibria also serve as examples of double symmetric tautomerism* Now note that any compound which contains a benzene nucleus (or condensed benzene nuclei) when considered from the standpoint of the electronic conception of positive and negative valence, will involve contraplex-diplex or absorption transitions within the primary and secondary systems of phasotropic equilibria of its electromers, and consequently must manifest one or more absorption bands in its spectrum. Now since fluorescence is produced only when the incident rays contain vibrations which the medium is capable of absorbing, it naturally follows that the function of the benzene nucleus in fluorescent compounds is to make possible the absorption of light as the result of the existence of contraplex-diplex transitions. Thus the three conditions noted above are correlated, and an explanation of the factor of absorption in the phenomenon of fluorescence is thereby afforded

The various theories on fluorescence and chemical constitution have failed to explain the factor of absorption in connection with the relations between the wave-lengths of the absorbed and the fluorescent or emitted light It has been shown that incident light of a given wave-length may excite a fluorescence consisting of several different rays, and, conversely, a given ray in the fluorescent spectrum may correspond to absorbed light of different wave-lengths. How are these facts to be interpreted in terms of contraplex-diplex transitions? In other words, what conditions in the making and breaking or rearrangement of contraplex and of diplex double bonds could be assumed to cause the emission of light of an oscillation frequency different from that which is absorbed? An answer to this question may be found in the following definitions of two possible types (I and II) of contraplex-diplex transitions.

Let A_1 and A_2 represent two electromers of a given compound in phasotropic equilibrium with one another. Also, let d_1 and d_2 be the number of diplex double bonds, and c_1 and c_2 be the number of contraplex double bonds in A_1 and A_2 respectively. Now if $d_1 = d_2$ and $c_1 = c_2$, then in the equilibrium $A_1 \rightleftharpoons A_2$ there would be no contraplex-diplex transitions, hence neither absorption of light nor fluorescence. On the other hand, if d_1 is unequal to d_2, or if c_1 is unequal to c_2, i e., $d_1 \neq d_2$, or $c_1 \neq c_2$, there would result two types (I. and II.) of contraplex-diplex transitions in the equilibrium $A_1 \rightleftharpoons A_2$.

Type I. When $d_1 = c_2$ and $c_1 = d_2$ the equilibrium $A_1 \rightleftharpoons A_2$ would involve contraplex-diplex transitions in which the number of diplex double bonds in one electromer is equal to the number of contraplex double bonds in the other electromer. In other words the number of diplex bonds in one electromer is balanced by an equal number of contraplex bonds in the other electromer Such a condition, fully described and exemplified in preceding chapters, constitutes the origin of a absorption band, that is the absorption of light of a definite oscillation frequency synchronous with the rate of transition from the one electromer to the other. For convenience in reference, contraplex-diplex transitions of this type have been and will be termed "absorption transitions"

Type II When $d_1 \neq c_2$, or $c_1 \neq d_2$, the equilibrium $A_1 \rightleftharpoons A_2$ will involve contraplex-diplex transitions in which either the number of diplex double bonds of the one electromer is unequal to the number of contraplex double bonds of the other electromer, or vice versa Such a condition could be productive of two results simultaneously (1) The absorption of light of a given frequency since some of the diplex or contraplex bonds of the one electromer are in equilibrium with, or are balanced by, an equal number of contraplex or diplex bonds, respectively, in the other electromer (2) The existence of a residual number of unbalanced double bonds which do not function in the absorption of light, must function in the emission of light of a frequency different from that which is absorbed, hence fluorescence. Contraplex-diplex transitions of this type (II.) will be termed "fluorescence transitions".

The several conditions described above may be summarized as follows —

When $c_1 = c_2$, and $d_1 = d_2$, the transition $A_1 \rightleftharpoons A_2$ causes neither absorption nor fluorescence

When $c_1 \neq c_2$, or $d_1 \neq d_2$, two types (I and II.) of contraplex-diplex transitions are possible

Type I. When $d_1 = c_2$ and $c_1 = d_2$, transition $A_1 \rightleftharpoons A_2$ produces absorption only.

Type II When $d_1 \neq c_2$, or $c_1 \neq d_2$, transition $A_1 \rightleftharpoons A_2$ occasions simultaneously, (1) absorption, and (2) emission of light, hence fluorescence

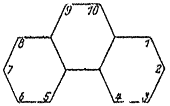
A general hypothesis may now be stated, namely, that *a substance manifests fluorescence whenever within the systems of dynamic equilibria of its electromers the number of diplex double bonds undergoing rearrangement is unequal to the number of contraplex double bonds simultaneously undergoing rearrangement*

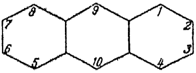
From the method of its development it is evident that *this hypothesis embodies the fundamental features of each of the previously noted theories.* It will now be extended to the dynamic formulæ and fluorescent spectra of anthracene and phenanthrene vapours.

C. Fluorescent Spectra of Anthracene and Phenanthrene.

Elston[113] has made an exhaustive study of the fluorescent and absorption spectra of anthracene and phenanthrene vapours and states that "the fluorescent spectrum of anthracene vapours consists of three bright bands at 390, 415, and 432 μμ superposed upon a continuous region extending from 365 to 470 μμ There is no evidence of lines When the fluorescent spectrum of pure phenanthrene vapour was photographed, it was found to consist of the same bands as that of anthracene, but with an additional band at 360 μμ" Elston then concludes that "there is an intimate connection between the fluorescence of the vapours of the two isomeric substances, undoubtedly due to their common chemical composition ($C_{14}H_{10}$) and similar structural composition . Just what gives rise to the extra band in the fluorescent spectrum of phenanthrene is not apparent"

Elston is undoubtedly correct in stating that there is an intimate connection between the fluorescence of the vapours of the two substances but this cannot be attributed entirely to their similar structural composition. While anthracene and phenanthrene each consists of three condensed benzene nuclei the position of the central nucleus in each formula renders them dissimilar A glance at the relative positions of carbon atoms 9 and 10 in each of the following formulæ makes evident the difference in structure:—





Anthracene and phenanthrene have three fluorescence bands in common. Elston states that the cause of the extra fluorescence band in the phenanthrene spectrum is not apparent. Now since these compounds are dissimilar in structure, it is natural to assume that the existence of the extra band is related in some way to this difference in structure. Hence in the application of the electronic conception of positive and negative valences to the constituent atoms of anthracene and phenanthrene, the purpose of the present chapter becomes threefold:—

(1) To show that within the systems of dynamic equilibria of the electromers of anthracene and phenanthrene there necessarily exist *fluorescence transitions.*

(2) To account for the existence of the extra band in the fluorescent spectrum of phenanthrene vapour

(3) To show that the oscillation frequencies of the fluorescence bands of anthracene and phenanthrene may be represented as linear functions of the numbers of fluorescence transitions occurring within the respective systems of dynamic equilibria of their electromers

The method of developing the electronic formulæ of benzene and naphthalene by symmetrically co-ordinating carbon atoms of types I and V, II and IV, and III. and III, has been applied to the constituent atoms of anthracene and phenanthrene. Two and only two centric electromers (A and B) of each of these compounds are derived. They are represented in Figs 12 and 13 respectively

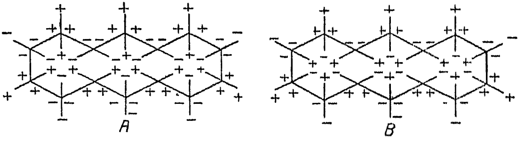


FIG. 12.

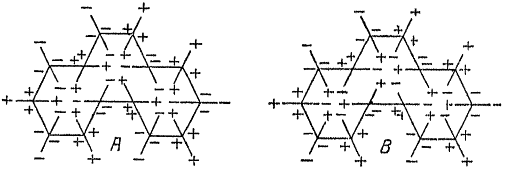


FIG 13

In each of the above figures the centric electromers (A) are composed of carbon atoms of the types I. and V while the centric electromers (B) embrace in their structure carbon atoms of the types II., III., and IV

D. Systems of Dynamic Equilibria of the Electromers of Anthracene.

A complete scheme of the several systems of dynamic equilibria of the electromers of anthracene is presented in Fig 14

Each electronic formula is the plane projection of a space formula The centric electromer A is the intermediate phase between the four possible phasotropic electromers, A^{I}, A^{II}, A^{III}, and A^{IV} By means of centric rearrangement A is convertible into B In turn, B functions as the intermediate phase between B^{I}, B^{II}, B^{III}, and B^{IV}.

The electromers of anthracene may be arranged into groups depending upon their respective symmetry and the number and kind of double bonds existing in their structure, thus —

A^{I}, A^{II},	each possessing	7 diplex double bonds, abbreviation	(7d)
A^{III}, A^{IV},	,, ,,	7 diplex double bonds, abbreviation	(7d)
B^{I}, B^{II},	,, ,,	7 contraplex double bonds, abbreviation	(7c)
B^{III}, B^{IV},	,, ,,	6 contraplex and 1 diplex bonds, abbreviation	(6c, 1d)

The primary and secondary systems of phasotropic equilibria which involve absorption and fluorescence transitions are included in the following table. (Note that the absorption transitions, such as $A^{I} \rightleftharpoons A \rightleftharpoons B \rightleftharpoons B^{I}$ and $A^{III} \rightleftharpoons A \rightleftharpoons B \rightleftharpoons B^{IV}$ are followed by a single asterisk The fluorescence transitions, such as $A^{I} \rightleftharpoons A \rightleftharpoons B \rightleftharpoons B^{III}$ and $B^{II} \rightleftharpoons B \rightleftharpoons B^{IV}$ involving the electromers B^{III} and B^{IV}, are followed by a double asterisk (**).)

Primary Systems

B^{I} —B—B^{III} **
(7c.) B^{I} —B—B^{IV} ** (6c., 1d)
B^{II}.—B—B^{III} **
B^{II} —B—B^{IV} **

Secondary Systems

A^{I} —A—B—B^{I} *
(7d.) A^{I}. —A—B—B^{II} * (7c.)
A^{II} —A—B—B^{I} *
A^{II} —A—B—B^{II} *

A^{I} —A—B—B^{III} **
(7d.) A^{I} —A—B—B^{IV} ** (6c., 1d.)
A^{II}. —A—B—B^{III} **
A^{II} —A—B—B^{IV} **

A^{III}.—A—B—B^{I} *
(7d.) A^{III} —A—B—B^{II} * (7c)
A^{IV}.—A—B—B^{I} *
A^{V}.—A—B—B^{II}. *

A^{III} —A—B—B^{III}. **
(7d.) A^{III}.—A—B—B^{IV} ** (6c., 1d)
A^{IV} —A—B—B^{III} **
A^{IV}.—A—B—B^{IV} **

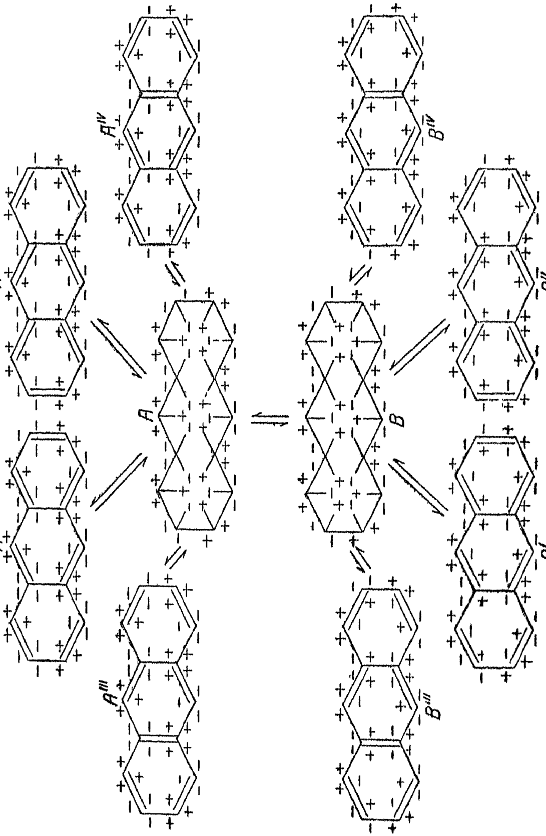


FIG. 14.

There are twelve fluorescence transitions within the complete system of dynamic equilibria of the electromers of anthracene

E. Systems of Dynamic Equilibria of the Electromers of Phenanthrene.

A complete scheme of the several electromers of phenanthrene in dynamic equilibria is presented in Fig 15

The centric electromer A is the intermediate phase between the five possible phasotropic electromers A^{I}, A^{II}, A^{III}, A^{IV}, and A^{V} By means of centric rearrangement A is convertible into B which functions as the intermediate phase between the electromers B^{I}, B^{II}, B^{III}, B^{IV}, and B^{V}

The electromers of phenanthrene may also be arranged into groups depending upon their respective symmetry and the number and kind of double bonds in their structure, thus ,—

A^{I}, A^{II},	each possessing	7 diplex	double bonds ,	abbreviation	(7d.)
A^{III}, A^{IV},	,, ,,	7 ,,	,, ,,	,,	(7d)
A^{V}	,,	7 ,,	,, ,,	,,	(7d)
B^{I}, B^{II},	,, ,,	7 contraplex	,, ,,	,,	(7c)
B^{III}, B^{IV},	,, ,,	6 ,,	and 1 diplex bond,	,,	(6c., 1d)
B^{V}	,,	5 ,,	,, 2 ,, bonds,	,,	(5c , 2d.)

It should be observed that an electromer of the type B^{V} containing five contraplex and two diplex double bonds is not to be found among the electromers of anthracene. Hence the existence of A^{V} and B^{V} in the phenanthrene system serves to distinguish it from the anthracene system, and furthermore must bear some relation to the additional fluorescence band in the spectrum of phenanthrene vapour.

The primary and secondary systems of phasotropic equilibria involving absorption and fluorescence transitions are included in the following table :—

Primary Systems

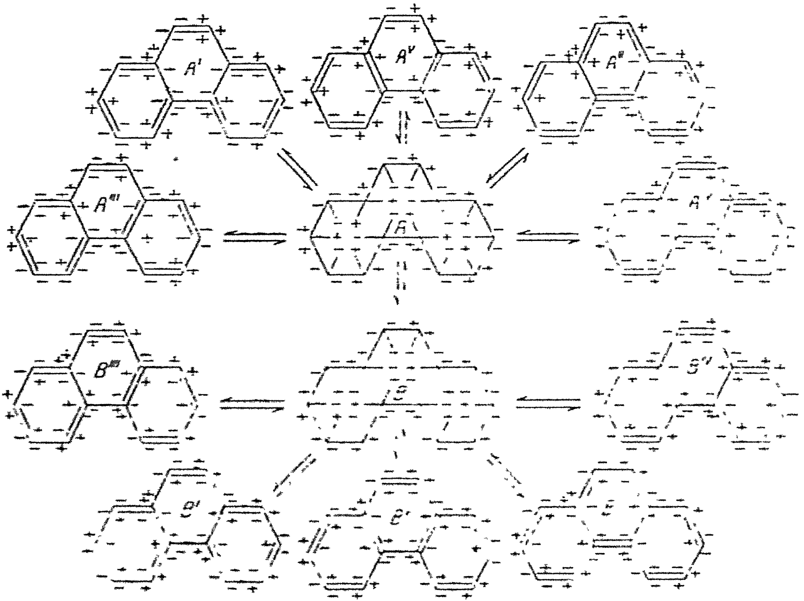
$$(7c.)\left\{\begin{array}{l} B^{I}\ —B—B^{III}\ ** \\ B^{I}\ —B—B^{IV}\ ** \\ B^{II}\ —B—B^{III}.\ ** \\ B^{II}\ —B—B^{IV}\ ** \end{array}\right\}(6c.,\ 1d.)$$

$$(7c.)\left\{\begin{array}{l} B^{I}.\ —B—B^{V}.\ ** \\ B^{II}\ —B—B^{V}\ ** \end{array}\right\}(5c.,\ 2d.)$$

$$(6c.,\ 1d.)\left\{\begin{array}{l} B^{III}.—B—B^{V}.\ ** \\ B^{IV}.—B—B^{V}.\ ** \end{array}\right\}(5c.,\ 2d\ )$$

Secondary Systems.

$$(7d.)\left\{\begin{array}{l} A^{I}.\ —A—B—B^{I}.\ * \\ A^{II}\ —A—B—B^{I}\ * \\ A^{I}\ —A—B—B^{II}.\ * \\ A^{II}.\ —A—B—B^{II}.\ * \end{array}\right\}(7c.)$$


A'
A^v
A''
A'''
A
B'''
B
B^v
B'
B'

$$(7d)\ \left\{\begin{matrix} A^{III}-A-B-B^{I} & * \\ A^{IV}-A-B-B^{I} & * \\ A^{III}-A-B-B^{II} & * \\ A^{IV}-A-B-B^{II} & * \end{matrix}\right\}\ (7c)$$

$$(7d)\ \left\{\begin{matrix} A^{V}-A-B-B^{I} & * \\ A^{V}-A-B-B^{II} & * \end{matrix}\right\}\ (7c)$$

$$(7d)\ \left\{\begin{matrix} A^{I}-A-B-B^{III} & ** \\ A^{II}-A-B-B^{III} & ** \\ A^{I}-A-B-B^{IV} & ** \\ A^{II}-A-B-B^{IV} & ** \end{matrix}\right\}\ (6c,\ 1d)$$

$$(7d)\ \left\{\begin{matrix} A^{III}-A-B-B^{III} & ** \\ A^{III}-A-B-B^{IV} & ** \\ A^{IV}-A-B-B^{III} & ** \\ A^{IV}-A-B-B^{I} & ** \end{matrix}\right\}\ (6c,\ 1d)$$

$$(7d.)\ \left\{\begin{matrix} A^{V}.-A-B-B^{III} & ** \\ A^{V}-A-B-B^{IV} & ** \end{matrix}\right\}\ (6c.,\ 1d)$$

$$(7d.)\ \left\{\begin{matrix} A^{I}-A-B-B^{V} & ** \\ A^{II}-A-B-B^{V} & ** \end{matrix}\right\}\ (5c,\ 2d)$$

$$(7d)\ \left\{\begin{matrix} A^{III}-A-B-B^{V} & ** \\ A^{IV}-A-B-B^{V} & ** \end{matrix}\right\}\ (5c,\ 2d)$$

$$(7d.)\ \{\ A^{V}-A-B-B^{V}\quad **\ \}\ (5c,\ 2d)$$

There are twenty-three fluorescence transitions within the system of dynamic equilibria of the electromers of phenanthrene, that is, eleven more than are to be found in the anthracene system This additional number of eleven transitions is made possible through the existence of the electromers A^{V} and B^{V}.

The first purpose of this chapter, namely, to demonstrate the existence of fluorescence transitions within the systems of phasotropic equilibria of the electromers of anthracene and phenanthrene, is realized in the preceding schemes of dynamic equilibria and tabulations thereof

The second purpose, namely, to account for the existence of the extra band in the fluorescent spectrum of phenanthrene vapour, is realized in the existence of the electromers A^{V} and B^{V} of the phenanthrene system. Electromer B^{V}, containing 5 contraplex and 2 diplex double bonds is a type which is not known in the anthracene system The existence of A^{V} and B^{V} makes possible eleven more fluorescence transitions in the phenanthrene system than in the anthracene system Hence these conditions, peculiar to the phenanthrene system, may naturally be assumed to constitute the explanation of the additional fluorescence band in the phenanthrene spectrum

F. The Correlation of Oscillation Frequencies of Fluorescence Bands and Fluorescence Transitions.

It now remains to be shown that the oscillation frequencies of the fluorescence bands of anthracene and phenanthrene may be represented as linear functions of the numbers of fluorescence transitions occurring in the systems of dynamic equilibria of their electromers The existence of such a relationship is to be expected since the oscillation frequencies of the absorption bands of benzene, chloro- and bromo-benzene and of naphthalene have been represented as linear functions of the numbers of absorption transitions occurring within the systems of equilibria of their electromers This relationship found expression in the equation for a straight line, $y = sx + b$, in which y is the oscillation frequency and x the number of absorption transitions

The oscillation frequencies of the fluorescence bands of anthracene and phenanthrene have been calculated from the values for the wave-lengths as determined by Elston and are embodied in the following table —

	Anthracene		Phenanthrene	
	λ	1/λ	λ	1/λ
Band One	432 μμ	2315	432 μμ	2315
,, Two	415 μμ	2410	415 μμ	2410
,, Three	390 μμ	2564	390 μμ	2564
,, Four	—	—	360 μμ	2778

The values for bands One, Two, and Three are identical for anthracene and phenanthrene

Heretofore the supposition has been made that all of the absorption transitions within a given system were synchronous with the light waves of highest oscillation frequency. Accordingly it may now be assumed that the maximum number of fluorescence transitions, namely, twelve in the anthracene system and twenty-three in the phenanthrene system, are respectively involved in the production of the anthracene fluorescence band Three (frequency 2564) and the phenanthrene fluorescence band Four (frequency 2778) How are the numbers of fluorescence transitions corresponding to, and functioning as the origin of, the oscillation frequencies of the remaining fluorescence bands of anthracene and phenanthrene to be determined?

In the following Fig 16, the oscillation frequencies are indicated on the Y-axis and the numbers of fluorescence transitions on the X-axis

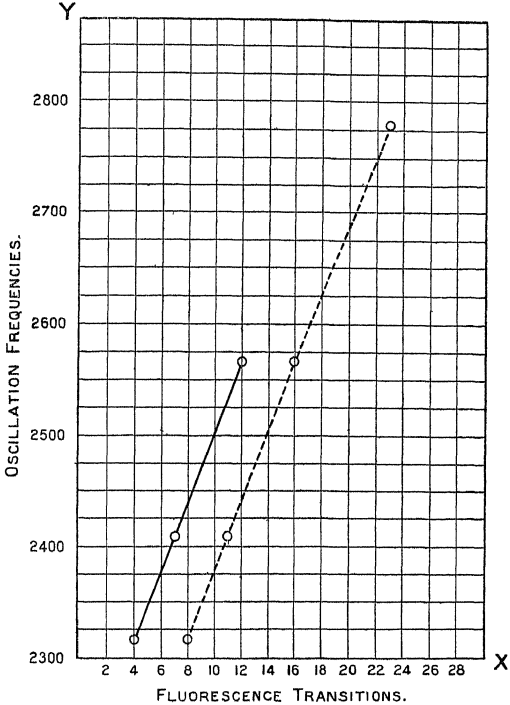


FIG 16.—Anthracene ——————————. Phenanthrene

An examination of the tabulated groups of transitions of the anthracene system shows that four (4) is the smallest number of fluorescence transitions comprising a group. If the vibrations of four such transitions are assumed to be synchronous with the lowest oscillation frequency (2315) of the anthracene fluorescence band One, and the vibrations of the maximum number of twelve transitions be synchronous with the highest oscillation frequency (2564) of anthracene fluorescence band Three, the points (4, 2315) and (12, 2564) will determine the direction of a straight line. Now note that this straight line intersects the perpendicular from the frequency value 2410, of band Two of anthracene, at a point which has a corresponding value on the X-axis equal to the whole number (7). Hence the oscillation frequencies 2315, 2410, and 2564, of the three fluorescence bands of anthracene may be represented as a linear function of the numbers of fluorescence transitions, 4, 7, and 12, respectively. The equation for the straight line which most nearly correlates these numbers with the corresponding frequencies, as determined by the method of least squares is—

$$y = 31.0918x + 2191.2959$$

in which y is the oscillation frequency of a given fluorescence band and x the number of fluorescence transitions functioning as its origin.

Does a similar relationship exist between the oscillation frequencies of the fluorescence bands of phenanthrene and a series of whole numbers of fluorescence transitions? Since the frequencies of the bands One, Two, Three, are identical for both anthracene and phenanthrene, it would naturally follow that the several whole numbers corresponding to the frequencies of the three bands of phenanthrene should differ by a constant quantity from the numbers 4, 7, and 12, which correspond to the frequencies of the three fluorescence bands of anthracene. Such a relationship could only be fulfilled when the expression for the linear function takes the form of an equation for a straight line *parallel* to the line for anthracene. In other words, the anthracene and phenanthrene lines must be parallel.

It has already been assumed that the twenty-three fluorescence transitions of the phenanthrene system correspond to the oscillation frequency 2778 of the phenanthrene fluorescence band Four. Now if a straight line be drawn through the point (23, 2778), parallel to the anthracene line (Fig. 16) it is remarkable that it practically intersects the perpendiculars from the frequency values on the Y-axis at points which have a corresponding value on the X-axis equal to the whole numbers 8, 11, and 16. In other words, the oscillation frequencies, 2315, 2410, 2564, and 2778, of the phenanthrene fluorescence bands may be represented as a linear function of the numbers of fluorescence transitions, 8, 11, 16, and 23, respectively. The equation for the straight line which correlates these numbers with the corresponding frequencies, as determined by the method of least squares, is

$$y = 30{\cdot}8255x + 2069{\cdot}7790,$$

in which y is the oscillation frequency of a given band, and x, the number of fluorescence transitions functioning as its origin.

The deviations of the calculated or theoretical values from the experimentally determined values of the oscillation frequencies of the fluorescence bands of anthracene and phenanthrene are embodied in the following tables:—

Anthracene: $y = 31{\cdot}0918x + 2191{\cdot}2959$

A	B	C	D
4	2315	2315·663	+ 0·663
7	2410	2408·938	− 1·061
12	2564	2564·397	+ 0·397

Phenanthrene: $y = 30{\cdot}8255x + 2069{\cdot}7790$

A	B.	C.	D
8	2315	2316·383	+ 1·383
11	2410	2408·859	− 1·141
16	2564	2562·987	− 1·013
23	2778	2778·765	+ 0·765

In the above tables columns (A) contain the theoretically determined numbers of fluorescence transitions represented by (x) in the linear equations for anthracene and phenanthrene, columns (B), the experimentally determined oscillation frequencies of the fluorescence bands represented by (y), columns (C), the frequencies as calculated from the anthracene and phenanthrene equations. Note that the deviations, in columns (D), of the calculated from the actual oscillation frequencies are so small that they may be attributed to errors in experimental observation.

These results substantiate the hypothesis that the oscillation frequencies of the fluorescence bands of both anthracene and phenanthrene may be represented as linear functions of the numbers of fluorescence transitions involved in the systems of dynamic equilibria of their respective electromers This fulfils the third object of the present chapter

It may now be of interest to compare Elston's electronic explanation of the fluorescent spectra of anthracene and phenanthrene with the hypothesis of fluorescence transitions Elston states that if we assume fluorescence to be produced by a system of electrons within the molecule, then, in order to account for the fluorescent spectrum of anthracene (or phenanthrene) vapour consisting of several bands superposed upon a continuous spectrum, we may consider either (1) that the electrons corresponding in period to the several bands are more numerous than those which give rise to the weaker continuous parts of the fluorescence, or (2) that the former are set in more violent vibration It may also be assumed (3) that the system of electrons is so intimately connected in its parts that, when disturbed by the exciting light in any manner, all of the electrons in the system are set in vibration If the disturbance of the system takes place through an intermediary "luminophore" then this luminophore undoubtedly consists of a connected system of electrons whose periods correspond to those of the absorption spectrum of the vapour

The proposed hypothesis of absorption and fluorescence transitions does away with the assumption of the "luminophore" or any other group of atoms, as the cause of fluorescence, and in its place presents a definite picture of the manner in which a system of electrons within the molecular structure of organic compounds may function so as to produce not only the absorption, but also the emission of light *All* of the several systems of electrons or electromers are intimately connected through the centric electromer and centric rearrangements If the system of electrons in a centric electromer be disturbed by the exciting light, phasotropic electromers are formed and thereby make possible the systems of dynamic equilibria which involve absorption and fluorescence transitions The existence of certain groups of transitions, the vibrations of which are synchronous with light waves of a definite oscillation frequency, constitutes the origin of absorption and fluorescence bands, the oscillation frequencies of which may be represented as linear functions of the numbers of absorption and fluorescence transitions respectively involved in their production

G. Other Interpretations by Means of Absorption and Fluorescence Transitions.

Other phenomena may be interpreted by the hypothesis of absorption and fluorescence transitions Stark and Meyer[141] have observed that for numerous benzene derivatives the regions of absorption lie adjacent to or overlap the regions of fluorescence Nichols and Merrit[145] also note that the broad continuous bands of fluorescent substances are always associated with a broad absorption band usually overlapping the fluorescence band on the side toward the violet, and that the absorption spectrum of the uranyl salts consists of a series of bands precisely similar, as regards their arrangement and number, to the bands of the fluorescence spectrum In the fluorescent spectrum of anthracene Elston observes that the bands are superposed upon a continuous region extending from $365\mu\mu$ to $470\mu\mu$, while the absorption spectrum extends continuously from about $400\mu\mu$ to some point beyond $325\mu\mu$ This relationship between the regions of absorption and fluorescence may readily be explained by the hypothesis of absorption and fluorescence transitions from two standpoints (1) A fluorescence transition, as previously defined, occasions absorption as well as the emission of light (2) A given type of electromer may often function both in an absorption transition, and in a fluorescence transition as is apparent in the tabulations of transitions on pages 241 and 243. Consequently the periods of vibration of these related absorption and fluorescence transitions must likewise be related. This phase of the subject merits further investigation and development

Finally, the relationship between fluorescence and phosphorescence, or luminescence, should be briefly considered Wood[146] states that a satisfactory theory of fluorescence must fulfil three requirements (1) It must distinguish between media which fluoresce, and those which do not. It must explain (2) the change in wave-length, and (3) the increase in duration of the emission, which is the phenomenon of phosphorescence. Wood further states that at present there is no satisfactory theory of fluorescence. The first two requirements of a satisfactory theory have been fulfilled in the development and application of the hypothesis of absorption and fluorescence transitions. The third requirement, namely, the explanation of phosphorescence may also be interpreted in terms of fluorescence transitions on the generally accepted assumption that the energy of the absorbed light is stored in the substance in the form of potential energy of the atoms. Now when the exciting source of light is removed, this potential energy, in order to be retransformed into radiant energy, causes a change in the positions of the electrons in the centric electromer. A disturbance of the condition of equilibrium in a centric electromer causes it to pass into its phasotropic electromers, and thereby a system of dynamic equilibrium is established which will involve fluorescence transitions. In other words, when the exciting source of light is withdrawn there is a continuation of the emission of light from the substance due to the persistence of fluorescence transitions which serve as the medium through which the potential energy of the absorbed light is transformed into fluorescent light.

A tentative explanation of the phosphorescence of mineral salts may also be given in terms of fluorescence transitions. It has been shown by several investigators that the action of ultra-violet light upon mineral salts causes dissociation and it has been assumed that after removal of the substance from the exciting source, phosphorescence is produced as the result of the recombination of the previously dissociated radicals. Now dissociation of a salt, MX, either into its ions $\overset{+}{M}$ and $\overset{-}{X}$, or molecularly into M and X, cannot occur unless there be a disturbance of the relative positions of the electrons and systems of electrons which constitute the radicals M and X (see p. 153). Hence the assumption may be made that the return to the undissociated condition, MX, is accompanied by changes which correspond in some way to fluorescence transitions.

While it is possible to give a definite picture of the rearrangements of valence electrons taking place within the molecules of such compounds as benzene, naphthalene, anthracene, and phenanthrene, it is not yet possible to extend the picture to the systems of electrons within an atom. The constitution of the atom is yet quite an enigma. Therefore it is probable that the knowledge of the relationship between absorption and fluorescence phenomena and chemical constitution will be advanced chiefly through the study of the dynamic equilibria of the electromers of various organic and inorganic compounds The absorption transition and fluorescence transition hypotheses cannot be applied to the atoms of elements because their electronic formulæ or structure is as yet unknown. Perhaps a study of the absorption and fluorescent spectra of the elements from the point of view of the numbers of contraplex-diplex transitions which possibly function as the origin of the absorption and fluorescence bands may shed some light upon the problem of the electronic constitution of the atom

PART IV.

METAL-AMMINES, BIBLIOGRAPHICAL REVIEW A GENERAL CONCLUSIONS

CHAPTER XXII

THE CONSTITUTION OF THE METAL AMMINES

A The Status of the Problem.

THE foremost problem of the organic chemist is generally conceded to be that of the constitution of benzene and substitution in the benzene nucleus Another perplexing problem, of lesser importance, but of equal interest, particularly to the inorganic chemist, is that of the constitution of molecular compounds, notably the metal-ammines

J W Mellor[117] states that "the attempt to distinguish molecular from atomic compounds, by structural formulæ based upon ordinary valencies deduced from the manifestations of the simple atomic compounds has not been successful". The significance of this statement is fully realized after one has attempted to comprehend and to correlate the various theories that have been proposed to explain the constitution of the metal-ammines Stewart[118] has presented a critical review of the foremost theories (as applied to the cobalt-ammines) notably those of Blomstrand, Jorgensen, Werner, Friend, Baker, and Ramsay. Hence a comprehensive review of these theories will not be attempted Stewart also concludes that the whole question of the constitution of the metal-ammines is at present in a very unsettled condition

On the other hand, Sir William Ramsay[119] maintains that no theory of valency would be acceptable if it did not *attempt* to assign structural formulæ to the metal-ammine compounds and to correlate their properties with their formulæ. Hence it is the purpose of the present chapter to attempt to apply the electronic conception of positive and negative valence as developed in this monograph to the constitution of the chief metal-ammines, namely, the platinous-ammonia, the platinic-ammonia, and the cobaltic-ammonia compounds.

It should be noted here that the theories of Friend and

Ramsay, and a later scheme of Nelson and Falk[150] are based upon the electron theory. Friend's system of formulation fails in its extension to the hexammine compounds since there is no valence to bind the hexatomic ring of six ammonia molecules to the remaining atoms of the compound molecule which are left suspended in space, so to speak. In Ramsay's electronic formulæ the ammonia molecules are singly bound to the central metal atom by a double bond of the contraplex type, i.e., the nitrogen atom of ammonia simultaneously gives to and receives from the metal atom an electron. This is the bringing into play of the so-called *latent valency* of Friend, identical with the *neutral affinity* of Spiegel and the *electrical double valence* of Arrhenius. Further, in Ramsay's electronic formulæ an ionizable atom or radical is attached to the nitrogen atom of an ammonia molecule which nitrogen atom is then bound by a single valence to the central or nuclear metal atom. This ionizable radical functions negatively. Nelson and Falk base their formulæ on the Werner co-ordination types. There are no new conceptions in the Nelson and Falk method of assigning electronic formulæ to the metal-ammines. The ammonia molecules and the ionizable radicals are united according to Ramsay's ideas.

In the present application of the electronic conception of valence to the constituent atoms of the metal-ammines, the Werner co-ordination formulæ and the various kinds of valency postulated and embodied therein, will not be considered. The chief reason for the rejection of the Werner co-ordination formulæ is due to the fact that the Werner-Jorgensen controversy, which extended over a period of eight years, has demonstrated that little can be gained by the wide departures of Werner from the old and well-tried system of valency as developed in relation to organic chemistry. Therefore, in the present chapter, the electronic conception of valence will be applied only to such structural formulæ for the metal-ammines as are in harmony with the principles of valency commonly employed in the writing of the structural formulæ of carbon compounds.

The structural and electronic formulæ herewith proposed will be derived through (1) the development of a few simple rules relative to the distribution of the positive and negative valences, and (2) the application of these rules to the empirical formulæ of the typical metal-ammines. To this end, the rational names and the empirical formulæ of the three foremost groups of metal-ammines will be tabulated as follows (A) the platinous-, (B) the cobaltic-, and (C) the platinic-ammonia compounds.

TABLE A

PLATINOUS-AMMONIA COMPOUNDS

	Rational Name	Empirical Formula	
1	Tetrammine-platinous salts	$[Pt(NH_3)_4]X_2$	
2	Triammine-platinous salts	$[Pt(NH_3)_3X]X$	
3	Diammine-platinous compounds	$[Pt(NH_3)_2X_2]$	(two isomers)

TABLE B

COBALTIC-AMMONIA COMPOUNDS

1	Hexammine-cobaltic salts	$[Co(NH_3)_6]X_3$	
2	Pentammine-cobaltic salts	$[Co(NH_3)_5X]X_2$	
3.	Tetrammine-cobaltic salts	$[Co(NH_3)_4X_2]X$	(two isomers)
4	Triammine-cobaltic compound	$[Co(NH_3)_3X_3]$	

TABLE C

PLATINIC-AMMONIA COMPOUNDS

1	Hexammine-platinic salts	$[Pt(NH_3)_6]X_4$	
2	Pentammine-platinic salts	$[Pt(NH_3)_5X]X_3$	(unknown)
3	Tetrammine-platinic salts	$[Pt(NH_3)_4X_2]X_2$	
4	Triammine-platinic salts	$[Pt(NH_3)_3X_3]X$	
5	Diammine-platinic compounds	$[Pt(NH_3)_2X_4]$	(two isomers)

In connection with the typical empirical formulæ noted in the above tables, it should be recalled that X, when located *within* the brackets, may represent a halogen atom, chlorine or bromine; a univalent radical, or a molecule of water or of halogen acid (HX), either of which molecules functions in the formula presumably in the same manner as does a molecule of ammonia. On the other hand, when X is *outside* the brackets it functions negatively as a univalent ionizable atom or radical From this it is also evident that the complex radical, i e, that part of the compound embodied within the brackets, functions positively as a univalent, a bivalent, a tervalent, or quadrivalent radical or ion according as the number of the univalent negative atoms of X outside the brackets is respectively X, X_2, X_3, or X_4.

B. Fundamental Principles Pertinent to the Electronic Formulæ of the Metal-Ammines

A survey of the three groups (A, B, and C) of metal-ammonia compounds reveals two remarkable relationships which constitute the basis for definite rules to be employed later in writing the electronic formulæ of metal-ammines. Relative to the development of the first relationship, note that in Table A there are *three* classes of platinous-ammonia compounds. In platinous compounds, platinum is *bivalent*. In Table B there are *four* classes of cobaltic-ammonia compounds. In cobaltic compounds, cobalt is *tervalent*. Lastly, in Table C, there are *five* classes of platinic-ammonia compounds. In platinic compounds, platinum is *quadrivalent*. In other words, when the valence of the metal atom of the metal-ammonia compound is (n), then there are (n + 1) classes of metal-ammines. In this connection recall the electronic valence rule previously developed and illustrated, namely, that when the valence of an atom is (n), that atom may function in electronic formulæ according to (n + 1) electronic types. The existence of this remarkable relationship between the numbers of classes of metal-ammines and the electronic valence rule leads to the immediate conclusion that *the number of classes of the metal-ammines of a given metal is related directly to the number of the electronic types in which said metal atom may function*. More specifically, the three classes of platinous-ammonia compounds noted in Table A correspond to the three electronic types —

$$\text{Pt}\,\overset{+}{+},\quad \text{Pt}\,\overset{+}{-},\ \text{and}\ \text{Pt}\,\overset{-}{-}$$

The four classes of cobaltic-ammonia compounds of Table B correspond to the four electronic types.—

$$\text{Co}\,\begin{matrix}+\\+\\+\end{matrix},\quad \text{Co}\,\begin{matrix}+\\+\\-\end{matrix},\quad \text{Co}\,\begin{matrix}+\\-\\-\end{matrix},\ \text{and}\ \text{Co}\,\begin{matrix}-\\-\\-\end{matrix}$$

Lastly, the five classes of platinic-ammonia compounds of Table C correspond to the five electronic types —

$$\text{Pt}\,\begin{matrix}+\\+\\+\\+\end{matrix},\quad \text{Pt}\,\begin{matrix}+\\+\\+\\-\end{matrix},\quad \text{Pt}\,\begin{matrix}+\\+\\-\\-\end{matrix},\quad \text{Pt}\,\begin{matrix}+\\-\\-\\-\end{matrix},\ \text{and}\ \text{Pt}\,\begin{matrix}-\\-\\-\\-\end{matrix}$$

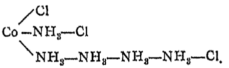
The second relationship is based upon the fact that some of the metal-ammines display ionogen properties while others do not. A definite correlation between the electronic type of the metal atom and the number of ionizable atoms or radicals (X) which exist in the compound is found in the fact that *the number of positive valences of the metal atom is equal to the number of the* *negative ionizable groups* (*X*) This principle makes it possible to relate a particular electronic type of the metal atom to a corresponding type of a metal-ammine. For example, in the platinous-ammine group, the tetrammine and the triammine salts display respectively *two* and *one* dissociable negative radicals (X) These numbers are equal to the numbers of positive valences of the metal atom, namely, *two* and *one*, which correspond respectively, to the electronic types $\mathrm{Pt}\ \overset{+}{+}$ and $\mathrm{Pt}\ \overset{+}{-}$. In this connection the diammine platinous compound displays no ionogen properties and, accordingly, its platinum atom, having no positive valences, conforms to the electronic type $\mathrm{Pt}\ \overset{-}{-}$

In the same manner, and according to the same principle, the four groups of cobaltic-ammines which display *three*, *two*, *one*, and *no* ionizable negative radicals, embody respectively cobalt atoms of the electronic types,

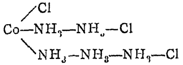
$$\mathrm{Co}\ \underset{+}{\overset{+}{+}},\ \mathrm{Co}\ \underset{-}{\overset{+}{+}},\ \mathrm{Co}\ \underset{-}{\overset{+}{-}},\ \text{and}\ \mathrm{Co}\ \underset{-}{\overset{-}{-}}$$

In other words, *the number of negative ionizable atoms or radicals of the metal-ammine is equal to the number of positive valences of the metal atom of the metal-ammine.* This relationship, found to hold for the platinous-, cobaltic-, and platinic-ammonia compounds, constitutes the second principle involved in the writing of the electronic formulæ of the metal-ammines

Before postulating the rules for writing the electronic formulæ of metal-ammines some account must be given of the manner in which the ammonia molecules are to be distributed It will be remembered that Blomstrand, and later Jorgensen, assumed a division of the ammonia molecules of the metal-ammines into chains by virtue of the ability of the nitrogen atom of ammonia to pass from its tervalent state to the quinquevalent condition. The pentammine-cobaltic salt was written thus :—



The non-ionizable chlorine atom is directly united to the cobalt atom, the two ionizable chlorine atoms are united to nitrogen and thus have the same ionogen properties as chlorine in ammonium chloride. Note that the above formula, comprising five ammonia molecules, has one chain of four ammonia molecules. Blomstrand and Jorgensen have advanced no reasons indicating how many ammonia molecules should be embodied in a nitrogen chain. Hence the above pentammine salt could be represented just as well by the following isomeric formula,



which contains chains of two and three ammonia molecules. In other words, the Blomstrand-Jorgensen method of assigning structural formulæ to the metal-ammines permits of more isomers than the facts warrant. To overcome this difficulty, which is also likely to be encountered in writing the electronic formulæ of metal-ammines, there must be some limitation and definition of the number of ammonia molecules to be embodied in a nitrogen chain.

To this end, a guiding principle is found in the fact that some metal-ammonia compounds, although generally stable, indicate a pronounced tendency to lose ammonia molecules *in pairs*. For example, in an atmosphere of ammonia at 760 mm pressure, the compound $Zn(NH_3)_6Cl_2$ decomposes at 59°, losing *two* molecules of ammonia, and in the same way the resulting compound $Zn(NH_3)_4Cl_2$ also loses *two* molecules of ammonia at 89.5° yielding $Zn(NH_3)_2Cl_2$. Finally, this compound decomposes at 269° with the loss of its remaining two molecules of ammonia. These transitions are summarized thus —

$$Zn(NH_3)_6Cl_2 \rightarrow Zn(NH_3)_4Cl_2 \rightarrow Zn(NH_3)_2Cl_2 \rightarrow ZnCl_2$$

Further evidence for the apparent association of groups of two molecules of ammonia in the metal-ammines is found in the fact that Magnus' Green Salt, $[(NH_3)_4Pt][PtCl_4]$, is made by the action of ammonia upon platinous chloride, $PtCl_2$. When boiled with ammonia it yields tetrammine-platinous chloride, $[Pt(NH_3)_4]Cl_2$. The tetrammine salts when heated also lose *two* molecules of ammonia yielding the symmetrical diammine compounds of general formula $[Pt(NH_3)_2Cl_2]$.

The pronounced tendency, noted in the foregoing facts, for ammonia molecules to enter into combination or to be eliminated from combination *in pairs*, warrants the assumption that *two* constitutes the number of ammonia molecules naturally occurring in a chain of ammonia molecules Therefore, in postulating rules for writing the structural and electronic formulæ of the metal-ammines, it will be assumed that not more than two molecules of ammonia will be embodied in a single nitrogen chain or chain of ammonia molecules

C. Rules for writing Structural and Electronic Formulæ of Metal-Ammines.

The rules for writing the structural and electronic formulæ of the metal-ammonia compounds noted in Tables A, B, and C (p 259) are as follows —

(1) Write all of the possible electronic types of the metal atom of the metal-ammines of a given metal When the valence of the metal is (n) there are ($n + 1$) electronic types and ($n + 1$) classes of metal-ammines

(2) Since the number of negative ionizable atoms or radicals (X) of the metal-ammine is equal to the number of positive valences of the metal, attach to each positive valence of the metal atom (M) a chain consisting of *two* molecules of ammonia and *one* atom or radical (X) which is ionizable and functions negatively, thus —

$$\mathrm{M}\overset{+\ \ -}{\text{——}}\mathrm{NH_3}\overset{+\ \ -}{\text{——}}\mathrm{NH_3}\overset{+\ \ -}{\text{——}}\mathrm{X}.$$

This electronic formula for the chain scheme may be abbreviated by indicating the polarity, omitting the valence line, and letting (a) represent a molecule of ammonia, thus —

$$\mathrm{M} + - a + - a + - \mathrm{X}.$$

In applying the above rule (2) it is quite evident that no more molecules of ammonia may be written into the electronic formula than actually exist in the empirical formula. However, *as far as the number of ammonia molecules will permit, this rule should be applied to each positive valence of the metal atom.*

If the metal-ammine contains an *odd* number of ammonia molecules it will be impossible to assign all of them in pairs Accordingly, the remaining odd number of ammonia molecules may be united *singly* to any negative valences of the metal atom, and these single ammonia molecules will in turn be united to an atom or radical X which functions positively, thus —

$$\mathrm{M} - + a - + \mathrm{X}.$$

It should be noted that when X is an acid radical, for example, chlorine or bromine, and is *positive*, it manifests little, if any, tendency to ionize. This is partly analogous to the situation presented by acids of the type $\overset{+}{\text{H}}\text{——}\overset{-}{\text{X}}$ and $\overset{+}{\text{H}}\text{——}\overset{-\quad -}{\text{O}}\text{——}\overset{+}{\text{X}}$ The tendency for X when negative to function as an anion is very pronounced, but when X is a non-metal and positive, its tendency to function as a cation is slight. (See Chapter VI on ionic amphoterism) On the other hand, if X is a metal its tendency to function positively as a cation is quite marked Apropos of the preceding statements the third rule is as follows —

(3) To each negative valence of the metal atom attach a chain consisting of *one* molecule of ammonia and one atom or radical X which will function positively, thus :—

$$\text{M} - + a - + \text{X}$$

If, in the application of rules (2) and (3) all of the available molecules of ammonia are distributed before all of the positive or negative valences of the metal atom are disposed of, the latter are united directly (without the interposition of ammonia molecules) to any remaining atoms or radicals, X If the remaining valence of the metal is positive, then X is negative, thus $\text{M} + - \text{X}$ If the remaining valence of the metal is negative, then X is positive, thus $\text{M} - + \text{X}$. This procedure maintains the principle previously noted that the number of the positive valences of the metal atom equals the number of negative atoms or radicals, while the number of negative valences of the metal atom equals the number of positive atoms or radicals

Before applying the above rules, the existence of isomers of the metal-ammines should be noted Their existence is correlated with the following rule (4) —

(4) Isomers are possible and are accounted for whenever in the application of the preceding rules there remain for disposition *one pair of negative valences* of the metal atom, *two molecules of ammonia*, and *two atoms or radicals which function positively* These may be disposed according to two structural electronic formulæ each of which (I) and (II), represents an isomer

$$\text{I}\quad \text{M}\begin{array}{l} - + a - + \text{X} \\ - + a - + \text{X} \end{array}$$

$$\text{II}\quad \text{M}\begin{array}{l} - + a - + a - + \text{X} \\ - + \text{X} \end{array}$$

Note that isomer I takes care of the negative valences of the metal atom according to rule (3) The possibility of another formula, isomer II, is somewhat exceptional in that a chain of two molecules of ammonia is united to a negative valence of the metal

Isomers of the following metal-ammines are known —

$$[\mathrm{Pta_2X_2}] \qquad [\mathrm{Pta_2X_4}] \qquad [\mathrm{Coa_4X_2}]\mathrm{X}$$

In these compounds the electronic types of the metal atoms are respectively as follows —

$$\mathrm{Pt}\begin{array}{l}-\\-\end{array} \qquad \mathrm{Pt}\begin{array}{l}-\\-\\-\\-\end{array} \qquad \mathrm{Co}\begin{array}{l}+\\-\\-\end{array}$$

In the application of the rules for writing the electronic formulæ of these compounds, there will remain for disposition in each, one pair of negative valences of the metal atom, two molecules of ammonia and two atoms, X_2, which are positive Hence the conditions exist for the two isomeric formulæ in conformity with rule (4) and the empirical facts.

D. Applications of the Rules.

The preceding rules (1-4) described and qualified, are based upon electronic principles established in conformity with empirical data They are, therefore, not to be regarded as arbitrary or hypothetical, but rather as affording a method of writing both the structural and the electronic formulæ of the metal-ammines. These rules will now be applied in the writing of the electronic formulæ of the platinous-, the cobaltic-, and the platinic-ammonia compounds. Their formulæ are recorded in tabular form. First, note that the empirical formulæ (taken in consecutive order from the preceding Tables A, B, and C of the metal-ammonia compounds) are immediately followed by the electronic formula or type of the metal atom in the given metal-ammine. These are followed by their electronic formulæ which are derived by an application of the foregoing rules to the positive and negative valences of the metal atoms.

TABLE A

PLATINOUS-AMMONIA COMPOUNDS

(1) $[\mathrm{Pta_4}]\mathrm{X_2}$	$\mathrm{Pt}\begin{array}{l}+\\+\end{array}$	$\mathrm{Pt}\begin{array}{l}+-a+-a+-x\\+-a+-a+-x\end{array}$
(2) $[\mathrm{Pta_3X}]\mathrm{X}$	$\mathrm{Pt}\begin{array}{l}+\\-\end{array}$	$\mathrm{Pt}\begin{array}{l}+-a+-a+-x\\-+a-+x\end{array}$
(3) $[\mathrm{Pta_2X_2}]$ (two isomers, I and II.)	$\mathrm{Pt}\begin{array}{l}-\\-\end{array}$	I $\mathrm{Pt}\begin{array}{l}-+a-+x\\-+a-+x\end{array}$ II $\mathrm{Pt}\begin{array}{l}-+a-+a-+x\\-+x\end{array}$

TABLE B

COBALTIC-AMMONIA COMPOUNDS

(1) $[\mathrm{Coa_6}]\mathrm{X_3}$	$\mathrm{Co}\begin{array}{l}+\\+\\+\end{array}$	$\mathrm{Co}\begin{array}{l}+-a+-a+-x\\+-a+-a+-x\\+-a+-a+-x\end{array}$
(2) $[\mathrm{Coa_5X}]\mathrm{X_2}$	$\mathrm{Co}\begin{array}{l}+\\+\\-\end{array}$	$\mathrm{Co}\begin{array}{l}+-a+-a+-x\\+-a+-a+-x\\-+a-+x\end{array}$
(3) $[\mathrm{Coa_4X_2}]\mathrm{X}$ (two isomers, I and II.)	$\mathrm{Co}\begin{array}{l}+\\-\\-\end{array}$	I $\mathrm{Co}\begin{array}{l}+-a+-a+-x\\-+x\\-+x\end{array}$ II $\mathrm{Co}\begin{array}{l}+-a+-a+-x\\-+a-+a-+x\\-+x\end{array}$
(4) $[\mathrm{Coa_3X_3}]$	$\mathrm{Co}\begin{array}{l}-\\-\\-\end{array}$	$\mathrm{Co}\begin{array}{l}-+a-+x\\-+a-+x\\-+a-+x\end{array}$

TABLE C

PLATINIC-AMMONIA COMPOUNDS

(1) $[\mathrm{Pta_6}]\mathrm{X_4}$	$\mathrm{Pt}\begin{array}{l}+\\+\\+\\+\end{array}$	$\mathrm{Pt}\begin{array}{l}+-a+-a+-x\\+-a+-a+-x\\+-a+-a+-x\\+-x\end{array}$
(2) $[\mathrm{Pta_5X}]\mathrm{X_3}$ (unknown)	$\mathrm{Pt}\begin{array}{l}+\\+\\+\\-\end{array}$	(Formula cannot be written in conformity with rules)
(3) $[\mathrm{Pta_4X_2}]\mathrm{X_2}$	$\mathrm{Pt}\begin{array}{l}+\\+\\-\\-\end{array}$	$\mathrm{Pt}\begin{array}{l}+-a+-a+-x\\+-a+-a+-x\\-+x\\-+x\end{array}$
(4) $[\mathrm{Pta_3X_3}]\mathrm{X}$	$\mathrm{Pt}\begin{array}{l}+\\-\\-\\-\end{array}$	$\mathrm{Pt}\begin{array}{l}+-a+-a+-x\\-+a-+x\\-+x\\-+x\end{array}$
(5) $[\mathrm{Pta_2X_4}]$ (two isomers, I and II.)	$\mathrm{Pt}\begin{array}{l}-\\-\\-\\-\end{array}$	I. $\mathrm{Pt}\begin{array}{l}-+a-+x\\-+a-+x\\-+x\\-+x\end{array}$ II $\mathrm{Pt}\begin{array}{l}-+a-+a-+x\\-+x\\-+x\\-+x\end{array}$

It is particularly noteworthy that no pentammine platinic salt of formula (2), Table C, namely $[\mathrm{Pt}a_5\mathrm{X}]\mathrm{X}_3$, is known The rules for writing the electronic formulæ are not applicable to a metal atom of the type $\mathrm{Pt}\begin{smallmatrix}+\\+\\+\\-\end{smallmatrix}$ because five molecules of ammonia cannot be attached in groups of two to each of the three positive valences of the metal An electronic formula may be written,

$$\mathrm{Pt}\begin{array}{l} +-a+-a+-x \\ +-a+-a+-x \\ +-a+-x \\ -+x \end{array}$$

but it is an exception to the rules which are applicable to each of the known metal-ammines The fact that this pentammine platinic salt does not exist, and that an electronic formula in conformity with the rules cannot be written, lends support to the proposed system of writing the structural and electronic formulæ of the metal-ammines.

It is also significant that the metal-ammine salts undergo electrolytic dissociation, that is, they ionize in aqueous solution, in conformity with the electronic formula When X is negative, it functions as an anion The remaining part of the molecule constitutes the cation, or positively charged complex radical For example, the ionic dissociation of the pentammine cobaltic salt is represented thus —

$$\mathrm{Co}\begin{array}{l} +-a+-a+-x \\ +-a+-a+-x \\ -+a-+x \end{array} \rightleftharpoons \left[\mathrm{Co}\begin{array}{l} +-a+-a \\ +-a+-a \\ -+a-+x \end{array}\right]^{\begin{smallmatrix}+\\+\end{smallmatrix}} + 2\overset{-}{\mathrm{X}}$$

These electronic formulæ suggest the possibility of explaining another type of electrolytic dissociation in which X is positive and functions as the cation The remaining part of the compound is the complex negative radical or anion (M = neutral atom)

$$\mathrm{M}\begin{array}{l} -+a-+x \\ +-a+-a+-x \\ +-a+-a+-x \end{array} \rightleftharpoons \overset{+}{\mathrm{X}} + \left[\mathrm{M}\begin{array}{l} -+a \\ +-a+-a+-x \\ +-a+-a+-x \end{array}\right]^{-}.$$

E. Metal-Ammines and Complex Salts: Transition Series.

This leads to an interpretation in terms of electronic formulæ of the series of seven cobaltic compounds in which the valence of the complex radical changes progressively from three positive to three negative The empirical formulæ of these compounds, recorded in the order of the noted transitions in valence of their complex radicals, are as follows:

$[Co(NH_3)_6]\,Cl_3$, $[Co(NH_3)_5(NO_2)]\,Cl_2$, $[Co(NH_3)_4(NO_2)_2]\,Cl$, $[Co(NH_3)_3(NO_2)_3]$, $K[Co(NH_3)_2(NO_2)_4]$, $K_2[Co(NH_3)(NO_2)_5]$, $K_3[Co(NO_2)_6]$

Before tabulating the electronic formulæ of this series of cobaltic compounds, the question of the disposition of the NO_2 groups must be considered. It should be recalled that the radical NO_2 may function either negatively or positively, according as it is looked upon as a derivative of $\overset{|}{H} . NO_2$, or $HO . \overset{|}{N}O_2$ respectively. Furthermore, NO_2 as a compound, or as an independent molecule, has been shown (p. 153) to function as a "free radical" in which the valence of its nitrogen atom is four. Accordingly, through the gain or through the loss of an electron it becomes a negative or a positive radical respectively. Since it may function as an independent molecule, there is nothing to preclude the assumption that chains of molecules of NO_2 may exist and function in the same manner as do chains of molecules of ammonia in the metal-ammines. Such chain formation is attributed to the capacity of the nitrogen atom, either of NH_3 or of NO_2, to part with and acquire simultaneously an electron, i.e., to develop a free positive and a free negative valence. Hence the following partial schemes show how (*a*) a negative atom may be at the end of a chain comprising two molecules of NH_3, and (*b*) how a positive atom may be at the end of a chain containing two molecules of NO_2:—

$$\begin{array}{lllll} (a) & M\ | & NH_3\ | & NH_3\ | & Cl; \\ (b) & M & |\ NO_2 & |\ NO_2 & |\ K. \end{array}$$

These arrangements maintain the rule that for every negative valence of the metal there shall be a positive atom, radical, or ion, and, for every positive valence of the metal there shall be a negative atom, radical, or ion.

The first column of the following table presents the empirical formulæ of the series of cobaltic compounds in question. The second column notes the magnitude and the polarity of the valence of the complex radical. Column three indicates the electronic type of the metal, followed, in the last column, by the electronic formula which is derived through an application of the previously developed rules and principles.

Number of Compound	Empirical Formula	Valence of the Complex Radical.	Electronic Type of Metal	Electronic Formula
(1)	$[Co(NH_3)_6]Cl_3$	3 +	$+$ $Co +$ $+$	$+ - NH_3 + - NH_3 + - Cl$ $Co + - NH_3 + - NH_3 + - Cl$ $+ - NH_3 + - NH_3 + - Cl$
(2)	$[Co(NH_3)_5(NO_2)]Cl_2$	2 +	$+$ $Co +$ $-$	$+ - NH_3 + - NH_3 + - Cl$ $Co + - NH_3 + - NH_3 + - Cl$ $- + NH_3 - + NO_2$
(3)	$[Co(NH_3)_4(NO_2)_2]Cl$	1 +	$+$ $Co -$ $-$	$+ - NH_3 + - NH_3 + - Cl$ $Co - + NH_3 - + NO_2$ $- + NH_3 - + NO_2$
(4)	$[Co(NH_3)_3(NO_2)_3]$	0	$-$ $Co -$ $-$	$- + NH_3 - + NO_2$ $Co - + NH_3 - + NO_2$ $- + NH_3 - + NO_2$
(5)	$[Co(NO_2)_6]K_3$	3 −	$-$ $Co -$ $-$	$- + NO_2 - + NO_2 - + K$ $Co - + NO_2 - + NO_2 - + K$ $- + NO_2 - + NO_2 - + K$
(6)	$[Co(NO_2)_5(NH_3)]K_2$	2 −	$-$ $Co -$ $+$	$- + NO_2 - + NO_2 - + K$ $Co - + NO_2 - + NO_2 - + K$ $+ - NH_3 + - NO_2$
(7)	$[Co(NO_2)_4(NH_3)_2]K$	1 −	$-$ $Co +$ $+$	$- + NO_2 - + NO_2 - + K$ $Co + - NH_3 + - NO_2$ $+ - NH_3 + - NO_2$
(8)	$[Co(NO_2)_3(NH_3)_3]$	0	$+$ $Co +$ $+$	$+ - NH_3 + - NO_2$ $Co + - NH_3 + - NO_2$ $+ - NH_3 + - NO_2$

A critical survey of the above table shows that the negative chlorine atoms (or ions) of compounds (1), (2), and (3), and the positive potassium atoms (or ions) of compounds (5), (6), and (7), are duly indicated in the electronic formulæ of the respective compounds. This correlates the ionogen properties of the compounds with their electronic formulæ.

The electronic formulæ of compounds (1), (2), (3), and (4) are in complete accord with the postulated rules and accordingly are perfectly similar, both structurally and electronically, to the formulæ of the cobaltic-ammonia compounds (1), (2), (3), and (4), respectively, of Table B (p. 266). Compounds (5), (6), and (7), however, embody NO_2 molecules, and NO_2 radicals, as previously explained. It should be noted that compounds (1) and (5), (2) and (6), (3) and (7), and (4) and (8), are perfectly similar *structurally*; but *electronically* there is a complete reversal of the polarity of the valences not only of the cobalt atoms, but also of the remaining molecules and radicals which comprise the compounds.

In this connection, it is remarkable that *structurally identical*, but *electronically opposite* formulæ, (4) and (8), are electronic isomers of the compound $[Co(NH_3)_3(NO_2)_3]$, *which is a non-electrolyte* In other words, formulæ (4) and (8) are *electromers* of the cobaltic-trinitro-triammine The existence of electromers of organic compounds has been demonstrated, i e, the reactions of certain compounds can be explained only by assuming the existence of its electromers, each of which enters into a definite chemical reaction yielding its own specific derivative The existence of electromers of inorganic compounds such as formulæ (4) and (8) is probable Such electromers may exist in tautomeric equilibrium (*electronic tautomerism*) or, if the properties of the compound so indicate, only in one electronic form Of the two possible formulæ, (4) is the more likely because its NO_2 radicals are positive and it is a non-electrolyte. This accords with the well-known fact that when the radical NO_2 is positive, it does not tend to function as an ion

The principles and rules presented in this chapter for writing the structural and electronic formulæ of the metal-ammines might be extended almost indefinitely to various other series of complex inorganic or molecular compounds, but enough has been given to suggest the possibility and the method of extension Whether the types of formulæ here proposed are more consistent and more significant than previously proposed formulæ for the metal-ammines is, of course, a question One claim, however, is made, namely, that the proposed electronic formulæ have not departed from the thoroughly established principles which underlie the writing of the structural and graphic formulæ of carbon compounds Furthermore, the electronic formulæ definitely qualify the valences as positive or negative and thereby effect more complete correlation with chemical properties

Since the electronic conception of positive and negative valence as applied to the constitution of benzene and many of its derivatives has made it possible to explain and to correlate many hitherto inexplicable and unrelated chemical and physico-chemical phenomena, it is to be hoped that the extension of the electronic conception of valence, as herewith applied to the constitution of the metal-ammines, may lead to a more complete development of the structural and electronic formulæ of both molecular and atomic compounds and thus bring them into a unified system

CHAPTER XXIII

BIBLIOGRAPHICAL REVIEW

A REVIEW of the contents of the many articles relating either directly or indirectly to the electronic conception of valence would require another volume. If, however, a review is limited to the published *applications* of the electronic conception of valence in so far as they relate to the interpretation and correlation of chemical and physico-chemical phenomena, it may be embodied conveniently in a single chapter. Accordingly the present chapter is limited to a *bibliographical* and *chronological* review of the applications of the electronic conception of valence presenting (1) the name (or names) of the author of the given article, (2) the title of the article, (3) the reference to the journal in which the article appeared, and (4) a brief abstract of the contents of the article.

A. Bibliographical Review of Published Applications.

The first applications of the electronic conception of valence to the interpretation of specific chemical phenomena by means of electronic formulæ were presented by H. S. Fry in a paper read before the Cincinnati Section of the American Chemical Society (January 15, 1908) entitled "An Hypothesis relative to ✓the Constitution of the Benzene Nucleus: an Application of the Corpuscular Atomic (Electronic) Conception of Positive and Negative Valences to the Constituent Atoms of Benzene," *J. Amer. Chem. Soc.*, **30**, 34 (1908). In this paper, Fry elaborated the electronic conception of positive and negative valence (originally suggested by Sir J. J. Thomson's work, *Electricity and Matter*), and proposed the new conceptions and terms *electromer*, *electronic tautomerism*, and the *electronic formula of benzene* with an explanation of the Brown and Gibson rule.

In the following year J. M. Nelson and K. G. Falk, also basing their views upon Thomson's hypothesis that the linkages between atoms in a compound are caused by the transfer of corpuscles, applied same to a number of facts chiefly from organic chemistry. "The Electronic Conception of Valency in Organic Chemistry," *School of Mines Quarterly*, **30**, 179-198 (1909). See also *J. Amer. Chem. Soc.*, **32**, 1637-1654 (1910), which practically embodies their first paper and gives a general discussion of aliphatic carbon and nitrogen compounds containing single, double, and triple bonds, compounds containing double bonds between unlike atoms; partial valence; and complex inorganic salts. In their summary, Nelson and Falk state that "all cases of isomerism connected with the presence of a double bond, whether between like or unlike atoms, have been referred to the direction of the valences of the double bond, instead of to spatial configurations as heretofore. The existence of certain isomers and the explanation of some hitherto unexplained reactions have also been referred to the direction of valences. The existence of 'partial valence' is shown to follow from the electric charges in a molecule."

H. S. Fry. "Die Konstitution des Benzols vom Standpunkte des korpuskular-atomistischen Begriffs der positiven und negativen Wertigkeit. I. Eine Interpretation der Regel von Crum Brown und Gibson." *Zeitschr. physikal. Chem.*, **76**, 385-397 (1911). The principles presented in this paper are embodied and further developed in Chapters II., VII., IX., and X. of this monograph.

H. S. Fry. *Idem.* II. "Dynamische Formeln und das Ultraviolettabsorptionsspektrum des Benzols". *Zeitschr. physikal. Chem.*, **76**, 398-412 (1911). See Chapter XVIII.

H. S. Fry. *Idem.* III. "Dynamische Formeln und das Ultraviolettabsorptionsspektrum des Naphtalins." *Zeitschr. physikal. Chem.*, **76**, 591-600 (1911). See Chapter XX.

K. G. Falk. "Electron Conception of Valence. II. The Organic Acids." *J. Amer. Chem. Soc.*, **33**, 1140-1152 (1911). Falk proposes a classification of the organic acids according to the direction of the valences by which the *alpha* carbon atom is combined with the other atoms of the molecule. The ionization constants ($K \times 10^5$) depend primarily upon the additive effects of the directive valences of this α-carbon atom: I. $\begin{smallmatrix}\rightarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}C\,.\,CO_2H$, ionization constants less than 0.01, II. $\begin{smallmatrix}\leftarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}C\,.\,CO_2H$, ionization constants 0 1 - 0 4, III $\leftrightarrows$ C CO_2H, ionization constants greater than 2

H S Fry "A Critical Survey of Some Recent Applications of the Electron Conception of Valence" *J Amer Chem Soc* ✓ **34,** 664-673 (1912) Fry maintains that Falk's classification of the organic acids is incomplete because it fails to take into account the direction of the valence which binds the α-carbon atom to the carboxyl group When this valence is considered, the theory demands eight classes of organic acids Falk postulates only four and considers experimental data for only three classes Furthermore the direction of the valence which binds the α-carbon atom to the carboxyl group, and which Falk ignores, is of prime importance because it determines whether the carboxyl group functions positively or negatively, i e, whether it corresponds electronically and chemically to the carboxyl radical in carbonic acid, or to the carboxyl radical in formic acid

W A Noyes "A Possible Explanation of Some Phenomena of Ionization by the Electron Theory" *J Amer Chem Soc*, ✓ **34,** 663 (1912) A short note also suggesting that ionization phenomena are related to the electronic state of certain atoms in the molecules of electrolytes

J M Nelson and K G Falk "The Electron Conception of Valence III Oxygen Compounds" *Communication, 8th International Congress of Applied Chemistry*, **6,** 212-221 (1912) An extension of their ideas to the oxygen atoms of certain compounds

H S Fry "Einige Anwendungen des Elektronbegriffs der positiven und negativen Wertigkeit IV Fluoreszenz Anthrazen und Phenanthren" *Zeitschr physikal Chem*, **80,** 29-49 (1912) See Chapter XXI

H. S Fry *Idem* V "Absorptionsspektra und dynamische Formeln von Chlor-, Brom- und Iod-benzol" *Zeitschr physikal. Chem*, **82,** 665-687 (1913) See Chapter XIX

W A Noyes "An Attempt to Prepare Nitro-nitrogen Trichloride, an Electromer of Ammono-nitrogen Trichloride". *J Amer Chem Soc*, **35,** 767-775 (1913) Ordinary nitrogen trichloride when titrated against arsenious acid is equivalent to six atoms of chlorine per molecule indicating that the formula is

$$\mathrm{N}\begin{array}{l} -\ +\ \mathrm{Cl} \\ -\ +\ \mathrm{Cl} \\ -\ +\ \mathrm{Cl} \end{array}$$

Noyes maintains that there should be an electromer of the formula,

$$N\begin{array}{l} + - Cl \\ + - Cl \\ + - Cl \end{array}$$

nitro-nitrogen trichloride, which would hydrolyze like other non-metallic chlorides to give nitrous and hydrochloric acids. To obtain this electromer, nitrosyl chloride and phosphorus pentachloride were brought together at 1000°-1100° to effect the reaction :—

$$NOCl + PCl_5 \rightarrow NCl_3 + POCl_3.$$

Much nitrosyl chloride remained unchanged. Chlorine and silicon tetrachloride were formed. Of thirty gas mixtures analysed, twelve obtained in six different experiments gave evidence of the formation of minute traces of the electromer nitro-nitrogen trichloride : 0.12-0.22 millimoles in a volume of about 70 cubic centimetres.

J. M. Nelson, H. T. Beans, and J. K. Falk. IV. "Classification of Chemical Reactions". *J. Amer. Chem. Soc.*, **35**, 1810-1821 (1913). ✓ The authors review and define more rigorously the terms and assumptions presented in their preceding papers. As more general than oxidation, the term *adduction* is proposed. On the basis of the electronic changes involved, chemical reactions are classified into oxidation-reduction changes, "onium" compound formation, and simple replacement or rearrangement. These classifications are illustrated by various electronic formulæ.

Two papers of related interest on "Valence and Tautomerism" should be noted. One was published by W. C. Bray and G. E. K. Branch, *J. Amer. Chem. Soc.*, **35**, 1440-1447 (1913), x the other by G. N. Lewis, *ibid.*, **35**, 1448-1455 (1913). Both papers deal chiefly with polemical and hypothetical distinctions, from the electronic point of view, between polar and non-polar valences.

K. G. Falk and J. M. Nelson. V. "Polar and Non-polar Valence". *J. Amer. Chem. Soc.*, **36**, 209-214 (1914). The authors oppose the view of Bray and Branch that valence is sometimes polar, sometimes non-polar, pointing out that in many cases, as in the Grignard reaction, we would, if that view is correct, have the two kinds of valence appearing in the same reaction. To make such a distinction is difficult, confusing, and unnecessary.

L W Jones "Applications of the Electronic Conception of Valence Part I Reactions among Certain Compounds containing Nitrogen. Part II The Beckmann Rearrangement" *Amer Chem J*, **50,** 414-443 (1913) Jones extends the electronic valence rule of Fry, namely, that when the valence of an atom equals (*n*) that atom may function in electronic formulæ in (*n* + 1) ways, to tervalent and to quinquevalent nitrogen atoms which present, respectively, four and six electronic types From the point of view of electronic oxidation-reduction reactions, many of which are intramolecular, the electronic types are displayed by and correlated with the chemical properties of amines, aldimes, nitriles, nitrile oxides, and many other nitrogen compounds Hydrolysis is the chief means of determining the state of oxidation of the nitrogen and carbon atoms Jones maintains "that a carbon atom when linked directly to a nitrogen atom does not readily take from it negative electrons, or, in other words, is not readily reduced by it". An inspection of all of the reactions classed as examples of the Beckmann rearrangement (including the Hofmann and Curtius reactions) shows that "in every case the rearrangement is accompanied by a process of intramolecular oxidation and reduction It seems very probable that this tendency of the system of linking carbon-nitrogen to pass to one in which the carbon atom is as fully oxidized as possible, and the nitrogen atom as fully reduced as possible may be the real determining factor in the Beckmann rearrangement, and that the formation of univalent nitrogen, proposed by Stieglitz as the immediate cause, may be a mere incident, necessary, to be sure, to pave the way for this change" An appreciation of the nature and extent of Jones' applications of the electronic conception of valence to the compounds of nitrogen requires a detailed study of the published paper.

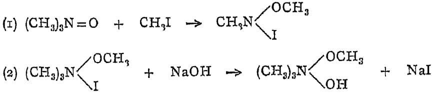
H S Fry. "Interpretations of Some Stereochemical Problems in terms of the Electronic Conception of Positive and Negative Valences. I Anomalous Behaviour of Certain Derivatives of Benzene" *J Amer. Chem Soc*, **36,** 248-262 (1914) See Chapter VIII

H. S Fry "Positive and Negative Hydrogen, the Electronic Formula of Benzene and the Nascent State". *J. Amer Chem Soc.*, **36,** 262-272 (1914) See Chapters IV and V.

Julius Stieglitz and P N Leach "The Molecular Rearrangement of Triarylmethyl-Hydroxyl-Amines and the 'Beckmann' Rearrangement of Ketoximes" *J Amer Chem Soc*, 36, 272-301 (1914) It is possible that the chloroimides obtained by Stieglitz and Peterson are electromers of the chloroimides supposed to be the intermediate products in the rearrangement of the ketoximes by phosphorus pentachloride Many rearrangement reactions are discussed in terms of the electronic valences of the nitrogen atom in relation to the positive and negative character of certain atoms and radicals Stieglitz, in presenting a new interpretation of the rearrangement of ketoximes, maintains that "with the change of electronic forces, the positive radical, *nearest to the field of force*, is lost by the now positive carbon and carried to the now negative nitrogen Such a series of actions would account for the nature and action of the reagents used to accomplish the rearrangement (acid dehydrating agents) and it gives a rational picture of the electrical forces in play in the rearrangement of the valences of the molecule Such a course would *also* account for the *influence* of *stereoisomerism* on the rearrangement, if such an influence should be established as beyond doubt—the radical nearest to the electrical fields of force produced by the migration of electrons from carbon to nitrogen passing under the influence of this force to the nitrogen." Again, it should be stated that an intimate study of the published paper necessarily precedes an appreciation of the proposed interpretations

L. W Jones. "Electromers and Stereomers with Positive and Negative Hydroxyl" *J. Amer Chem Soc.*, 36, 1268-1290 (1914) Jones cites experimental facts which he believes are sufficient not only to establish a tautomeric relationship between hydroxylamine and its derivatives in the ordinary structural sense but also to confirm the belief that these compounds in many of their reactions behave tautomerically in the electronic sense, i e, afford examples of electronic tautomerism The paper deals in particular with· (1) structural tautomerism of hydroxylamine derivatives, (2) oxidation and reduction of hydroxylamine and its derivatives, (3) the action of hypochlorous acid and bromine upon tertiary amines, (4) an electronic explanation of these actions, (5) electronic tautomerism of hydroxylamine and its derivatives, and (6) electromers and stereomers with positive and negative hydroxyl, or alkoxyl In the last section, Jones *shows conclusively that certain derivatives of hydroxylamine*, prepared by Meisenheimer, are *electromers* The following quotations taken freely from a subsequent paper by Jones (*Science*, Vol 46, No 195, 493-502) presenting this same phase of the subject, are of moment ·—

"In an article concerning the 'Non-Equivalence of the Five Valences of Nitrogen,' Meisenheimer describes the preparation of two isomeric compounds of the type, $(R)_3N(OCH_3)(OH)$ The *first* isomer was obtained by the action of (1) methyl iodide upon trimethylamine oxide and (2) subsequent replacement of iodine by hydroxyl Thus —

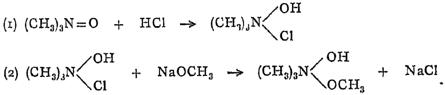


$$(1)\ (CH_3)_3N{=}O + CH_3I \rightarrow CH_3N\begin{matrix}OCH_3\\I\end{matrix}$$

$$(2)\ (CH_3)_3N\begin{matrix}OCH_3\\I\end{matrix} + NaOH \rightarrow (CH_3)_3N\begin{matrix}OCH_3\\OH\end{matrix} + NaI$$

(A)

"The *second* isomer was secured by the action of sodium methylate upon the salt obtained by treating trimethylarylamine oxide with hydrogen chloride —

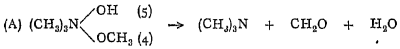


$$(1)\ (CH_3)_3N{=}O + HCl \rightarrow (CH_3)_3N\begin{matrix}OH\\Cl\end{matrix}$$

$$(2)\ (CH_3)_3N\begin{matrix}OH\\Cl\end{matrix} + NaOCH_3 \rightarrow (CH_3)_3N\begin{matrix}OH\\OCH_3\end{matrix} + NaCl.$$

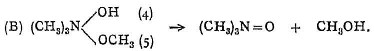
(B)

The two forms, (A) and (B), are identical *except for the order in which the hydroxyl groups and the methoxyl groups are introduced* In (B), as Meisenheimer said, the methoxyl group is linked to the '*fifth* valence,' or the one which usually engages the *acid radical*, while it is linked to the '*fourth* valence' in formula (A). But these two substances (structural isomers) are fundamentally different When an aqueous solution of (A) was heated, it decomposed quantitatively according to the equation —



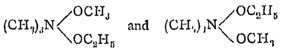
$$(A)\ (CH_3)_3N\begin{matrix}OH\ (5)\\OCH_3\ (4)\end{matrix} \rightarrow (CH_3)_3N + CH_2O + H_2O.$$

The trimethylhydroxyammonium methylate (B) showed a totally different behaviour —



$$(B)\ (CH_3)_3N\begin{matrix}OH\ (4)\\OCH_3\ (5)\end{matrix} \rightarrow (CH_3)_3N{=}O + CH_3OH.$$

"In addition to these compounds, Meisenheimer prepared a number of isomeric mixed dialkyl compounds with methyl, ethyl, and propyl radicals, e g.—



$$(CH_3)_3N\begin{array}{l}OCH_3\\OC_2H_5\end{array} \quad \text{and} \quad (CH_3)_3N\begin{array}{l}OC_2H_5\\OCH_3\end{array}$$

In every case, water decomposed compounds of this type to give a tertiary amine, an alcohol, and an aldehyde, but, invariably, the radical eliminated as aldehyde was the radical which occupied 'position four (4),' and the group eliminated as alcohol always occupied 'position five (5)' Meisenheimer stated that he never obtained recognizable traces of the aldehyde which should have resulted if the group attached in position five had separated in that form

"The electronic conception of valence fully explains these disputed relations by assuming that the one hydroxyl (or alkoxyl) group (4) is positive while the other (5) is negative Thus ·—

$$(A)\ (CH_3)_3N \begin{array}{l} -\ +\ O\ -\ +\ CH_3\ (4) \\ +\ -\ O\ -\ +\ H\ \ \ \ \ (5) \end{array} \rightarrow (CH_3)_3N \begin{array}{l} -\ +\ H \\ +\ -\ O\ -\ +\ H \end{array} + \left(H_2C \begin{smallmatrix}-\\+\end{smallmatrix} \begin{smallmatrix}+\\-\end{smallmatrix} O\right)$$

$$(B)\ (CH_3)_3N \begin{array}{l} -\ +\ O\ -\ +\ H\ \ \ \ \ (4) \\ +\ -\ O\ -\ +\ CH_3\ (5) \end{array} \rightarrow (CH_3)_3N \begin{smallmatrix}-\\+\end{smallmatrix} \begin{smallmatrix}+\\-\end{smallmatrix} O + (CH_3 + - O - + H).$$

"It is significant that the two oxygen atoms upon which the existence of the electromers depends are not linked directly to each other but through an intermediate atom, nitrogen, thus ·—

$$(RO + - N + - OH) \quad \text{and} \quad (HO + - N + - OR).$$

Jones maintains that this is undoubtedly responsible for the relative stability of these electromers as compared with others in which the atoms of different polarity are directly connected, e.g —

$$\overset{+\ -}{A\text{——}B} \quad \text{and} \quad \overset{-\ +}{A\text{——}B}\text{"}$$

H S Fry. "Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences. II. Halogen Substitution in the Benzene Nucleus and in the Side Chain." *J. Amer. Chem. Soc.*, **36**, 1035-1047 (1914) See Chapter XV.

J. M. Nelson and K. G. Falk: "The Electron Conception of Valence VI. Inorganic Compounds" *J. Amer. Chem. Soc.*, **37**, 274-286 (1915) Applications are extended to Werner's conceptions. The authors adopt th

relative to the electronic constitution of the cobaltic-ammines and extend same to platinic-ammines Werner's co-ordination formulæ are the structural basis for the electronic formulæ of the metal-ammines as conceived by Ramsay and later by Nelson and Falk

H S Fry "Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences III A Continuation of the Interpretation of the Brown and Gibson Rule" *J Amer Chem Soc*, **37**, 855-863 (1915) See Chapter IX

H S Fry. *Idem.* IV "The Simultaneous Formation of Ortho-, Meta-, and Para-Substituted Derivatives of Benzene" *J Amer Chem Soc*, **37**, 863-883 (1915) See Chapter XI

H S Fry *Idem* V. "A Reply to A. F Holleman" *J Amer Chem Soc*, **37**, 883-892 (1915)

K G Falk and J. M Nelson. "Electron Conception of Valence VII. Theory of Electrolytic Dissociation and Chemical Action" *J Amer Chem Soc*, **37**, 1732-1748 (1915) The authors hold that changes occurring in chemical reactions do not depend upon the electrolytic dissociation of the reacting substances The chemical changes are accompanied very often by electrolytic dissociation phenomena but the latter parallel the former, or vice versâ, and do not necessarily precede or cause them

H S Fry. "Einige Anwendungen der elektronischen Auffassung positiver und negativer Valenzen VI. Uber die Existenz und die Eigenschaften 'freier Radikale'" *Zeitschr physikal Chem*, **90**, 458-480 (1915) See Chapter XVI

H S Fry "Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences VI Further Evidence for the Electronic Formula of Benzene and the Substitution Rule" *J. Amer Chem Soc*, **38**, 1323-1327 (1916) See Chapter VIII

H. S. Fry *Idem.* VII "The Action of Sodium Methylate upon the Products of Nitration of Ortho-, Para-, and Meta-Chlorotoluenes" *J Amer Chem Soc.*, **38**, 1327-1333 (1916). See Chapter XII

H S Fry. *Idem* VIII "Further Evidence for the Electronic Tautomerism of Benzene Derivatives" *J Amer. Chem Soc*, **38**, 1333-1338 (1916) See Chapter X.

H S Fry. *Idem* IX "The Electronic Formula of Benzene and the Molecular Volumes of the Chlorobenzenes" *J Amer Chem Soc*, 39, 1688-1699 (1917) See Chapter XVII

L W Jones. "Electromerism, A Case of Chemical Isomerism resulting from a Difference in Distribution of Valence Electrons". *Science*, Vol XLVI., No 1195 (1917) The essential features of this paper have been reviewed in the abstract of Jones' paper on "Electromers and Stereomers with Positive and Negative Hydroxyl" (p 277)

M T Hanke and K K. Koessler. "The Electronic Constitution of Acetoacetic and Citric Acids and some of their Derivatives" *J Amer Chem Soc.*, 40, 1726-1732 (1918) When citric acid is treated with fuming sulphuric acid the central carboxyl group escapes as carbon monoxide The reason for the elimination of the central carboxyl group and the non-elimination of the two end carboxyl groups is due to a difference in the direction of the valence force holding these groups In other words, as Fry has shown, the elimination of a carboxyl group as carbon monoxide signifies that said group functions negatively Its carbon atom corresponds to the state of oxidation and the electronic type of the carbon atom in formic acid, which readily yields carbon monoxide Citric acid, losing carbon monoxide, yields acetone dicarbonic acid which contains the two end carboxyl groups of the original citric acid These are eliminated as carbon dioxide on treatment with caustic alkali solution, yielding acetone Again, as Fry has shown, the elimination of a carboxyl group as carbon dioxide shows that said carboxyl group functions positively Its carbon atom corresponds to the state of oxidation and to the electronic type of the carbon atom in carbonic acid, which loses carbon dioxide By the application of these principles, Hanke and Koessler are able to propose electronic formulæ for various complex acids which are readily correlated with their chemical properties.

Rajendralal De: "Polar and Non-Polar Valency". *Trans. Chem Soc*, **115**, 127-134 (1919) In the light of recent theories of atomic structure, De has discussed the structural significance of complex salts such as the cobalt- and platinum-ammonia compounds, acetylides, etc, in relation to polar and non-polar valency

Eustace J. Cuy: "The Electronic Constitution of Normal

Carbon Chain Compounds, Saturated and Unsaturated" *J Amer Chem Soc*, **42**, 503-514 (1920) Cuy summarizes his paper thus "Assuming that carbon compounds are polar in nature and that carbon atoms in a chain tend to assume alternately positive and negative charges, it has been shown that the fluctuation in the various physical properties of these compounds such as melting points, boiling points, and so forth, between the even and the odd members of a given series, may be accounted for Various reactions in which these compounds take part, such as the addition of halogen acids and the isomeric rearrangement of the halides may likewise be accounted for, on the basis of these assumptions"

Many significant papers have not been noted in the foregoing review for the reason that they are concerned chiefly with the problem of the constitution of the atom While they bear more or less directly upon the question of chemical valence, they are not primarily direct applications of the electronic conception of valence to the interpretation of specific chemical reactions In this connection the following papers should be noted .—

G N Lewis. "The Atom and the Molecule" *J. Amer Chem Soc.*, **38**, 762-784 (1916)

G N. Lewis "Steric Hindrance and the Existence of Odd Molecules (Free Radicals)" *Proc Nat Acad Sci*, **2**, 586 592 (1916)

Irving Langmuir "The Arrangement of Electrons in Atoms and Molecules" *J Amer Chem Soc*, **41**, 868-934 (1919)

Irving Langmuir "Isomorphism, Isosterism, and Covalence" *J Amer Chem Soc*, **41**, 1543-1559 (1919)

Irving Langmuir "The Structure of Atoms and Its Bearing on Chemical Valence" *J Ind Eng Chem*, **12**, 386-388 (1920).

The atomic configurations and methods of representing electronic valences presented in these and many other papers are so complicated that they do not lend themselves readily to a convenient form of graphic or structural illustration when one attempts to make application to specific chemical reactions In other words, their adaptability to *elucidate* structural formulæ and chemical reactions is questionable.

B. Review of Criticisms.

The introduction of the electronic conception of valence and its extension to the interpretation of chemical phenomena has met with some criticism The papers embodying these criticisms should be noted briefly in this bibliographical review

P de Heen · "The Electron Theory and Conception of Valence" *Bull. Acad Roy Belg*, **1913**, 667-679 The author's chief criticism is that the electron theory does not furnish any satisfactory account of the behaviour of the elements of variable valency. To this it may be replied that when the valence of an element is (*n*) that element may function electronically in (*n* + 1) ways If the ordinary valence varies, the same rule applies as well to the one value for (*n*) as to the other value or valence (*n*) Numerous illustrations of this rule have been given in this monograph. Jones (loc cit) has indicated methods of considering electronically the nitrogen atom which may function either as a tervalent or a quinquevalent element

S J Bates "The Electron Conception of Valence" *J Amer Chem Soc*, **36**, 789-793 (1914) Bates maintains that "on the whole the phenomena of physics are opposed to the view that in the molecule the atoms are charged with respect to one another, and to the theory of valence developed on this assumption. Chemistry contributes the most satisfactory evidence in its favour" This type of criticism is irrelevant for two reasons (1) The isolated conditions under which the quoted physical phenomena are effected (e g, high vacua, influence of positive rays, etc) are not comparable with the conditions under which the great majority of chemical reactions take place. Therefore, both the results and conclusions are bound to differ (2) The electronic conception of positive and negative valence plays the part of *a formulative hypothesis* in the interpretation and correlation of chemical and physico-chemical phenomena.

A F Holleman. "Substitution in the Benzene Nucleus" *J. Amer Chem Soc*, **36**, 2495-2498 (1914) Holleman maintains that there is no hypothesis able to give a satisfactory explanation of the phenomena of substitution in the benzene nucleus He states that Fry's electronic formula for benzene and rule for the explanation of substitution reactions cannot be accepted "because there are so many objections to it". He presents six "most important" specific objections which should be studied intimately by the reader Fry has replied in detail to each of these objections, *J Amer Chem Soc*, **37**, 883-892 ✓(1915), showing by direct quotations from Holleman's criticism and Fry's original statements that Holleman's inability to correlate Fry's rule with certain cases of substitution was due to Holleman's failure to apply to the principle of the electronic tautomerism of benzene derivatives the generally accepted principle that, in any tautomeric equilibrium mixture, either one, or the other, or both tautomers (depending upon conditions) may interact with a given reagent Thus the simultaneous formation of ortho-, para-, and meta-substituted derivatives is readily explained Furthermore, those cases of substitution which Holleman regarded as opposed to Fry's rule were shown to conform to the rule and to the principle of the electronic tautomerism of benzene derivatives An appreciation of the points at issue between Holleman and Fry necessitates a critical study of their original papers. It is of interest to add that in a private communication from Professor A F Holleman (Amsterdam, June 7, 1915), he writes "I fear that you have gone too far in your explanations, and it will be necessary to review your hypotheses, though I acknowledge that there is a right nucleus in them" While Holleman apparently did not completely sense the significance of the principle of electronic tautomerism and the necessary part it plays in substitution reactions, J B Cohen[151] clearly states the principle in his review of Fry's electronic theory of benzene substitution Cohen concludes his summary with the statement that Fry's theory, "in short, is so mobile, so adaptable, and so ingeniously applied as to explain most of the facts of substitution as well as many reactions of aromatic compounds"

R F Brunel · "A Criticism of the Electron Conception of Valence" *J Amer Chem Soc*, **37**, 709-722 (1915) Brunel concludes that any application of the theory involves the constant use of assumptions, that the electronic formulæ assigned to chemical compounds are inconsistent with any rule that can be proposed, that no single well-established case of electromerism is yet known, and that the evidence of physical experiments is at present opposed to the assumption on which it is based.

H S Fry "The Electronic Conception of Positive and

Negative Valences". *J. Amer Chem Soc*, 37, 2368-2373 (1915) A reply to the preceding paper of Brunel

There now remains for consideration a brief discussion of the status and functions of the electronic conception of positive and negative valence This is the subject of the concluding chapter

CHAPTER XXIV.

THE STATUS AND FUNCTION OF THE ELECTRONIC CONCEPTION OF POSITIVE AND NEGATIVE VALENCE

THE final chapter of *Recent Advances in Organic Chemistry* by A W. Stewart[152] discusses "modern formulæ and their failings". The introductory paragraph bears the following statement "An unbiased survey of the fields covered by organic chemistry cannot fail to reveal to any critical mind the fact that our structural formulæ are becoming less and less able to cope with the strain which modern research is placing upon them It is true that for work-a-day purposes they still answer admirably, and from the point of view of teaching it is doubtful if anything better could be devised. But when we go into the matter beyond the mere surface, things are not so satisfactory as they may appear to the superficial observer"

Examples are cited by Stewart to show that our formulæ have ceased to be pure "reaction-formulæ" and that they frequently mislead us if we attempt to draw general conclusions from them On the other hand, researches in physics and physical chemistry are giving us glimpses of the "intimate structure of molecules" Therefore, a difficult task is encountered when one attempts to embody reaction-formulæ and intimate structure of molecules simultaneously in one configuration Stewart admits that progress along these lines will be slow, but it is the task of investigators who concern themselves with both physical and chemical properties to invent a special symbolism which will express their results and be free from the implications that are attached to ordinary formulæ "Conservatism is ingrained in most scientific minds, and the struggle which new ideas have before them is generally severe"

A. Status and Function of the Electronic Conception of Valence.

Apropos of the foregoing points of view of Stewart, what is the *status* and *function* of the electronic conception of positive and negative valence and the new types of formulæ—electronic formulæ—proposed, developed, and illustrated in this monograph? The answer to this question is manifold

(1) It should be recalled that the electronic conception of positive and negative valence, as noted in the introduction (Chapter I) is a formulative hypothesis It is maintained that it should function as such in the interpretation and correlation of chemical and physico-chemical phenomena

(2) The electronic conception of positive and negative valence as herewith applied to the constituent atoms of relatively well-established structural formulæ, is, at its present status of development, neither primarily nor necessarily concerned with the question of the ultimate nature of chemical affinity and the constitution of the atom *per se* Such questions have invariably led into fields wherein speculation predominates Moreover, the numerous, varied, and divergent hypotheses relating to the ultimate constitution of the atom have failed, so far, to furnish a uniformly satisfactory valence hypothesis which will enable chemists to elucidate chemical formulæ and reactions.

The most to be gleaned from any or all of these anomalous hypotheses is the early and relatively simple suggestion of Sir J J Thomson that "if we interpret the 'bond' of the chemist as indicating a unit Faraday tube, connecting charged atoms in the molecule, the structural formulæ of the chemist can be at once translated into the electrical theory". Thus, in the electronic theory, one end of a bond corresponds to a positive, the other to a negative charge, the charge being developed through the loss or the gain of an electron It is this earlier view that is most readily and significantly adaptable to chemical formulæ. Later views on the electronic nature of valence and the distribution of valence electrons have manifested little, if any, discernible utility in the direct and lucid interpretation of the mechanism of specific chemical reactions and the correlation of the varied phenomena of inorganic and organic chemistry

(3) It should also be recalled that the translation of a structural formula into an electronic formula is not an arbitrary procedure Many illustrations have been presented showing that this translation is governed by a careful study of the phenomena of ionization and electrolysis, oxidation-reduction processes, and hydrolytic reactions. Each of these phenomena is readily

interpreted in terms of electric charges, that is, positive and negative valences or the capacity of atoms and radicals to function positively and negatively It is in conformity with these physical and chemical phenomena that the polarity of the valences or bonds in a structural formula are indicated by plus and minus signs thus making the translation of a structural formula into an electronic formula both a physically and a chemically consistent procedure

(4) Many substituted derivatives of benzene when singly brought into hydrolytic reactions, or subjected to further substitution, yield derivatives whose existence and properties compel us to conclude that the reaction involved more than one type of molecule of the initial benzene derivative These molecules are not those of tautomers or desmotropes They are electronic tautomers, or electromers, existing in tautomeric equilibrium, that is, manifesting the phenomenon of electronic tautomerism If this assumption, the principle of electronic tautomerism, is not valid, then we are still unable to explain either the simultaneous formation of ortho-, meta-, and para-derivatives of benzene in any given substitution reaction or the chemical properties of the substituted derivatives formed which are the specific products of respective electromers While the isolation of the electromer of any benzene derivative has not as yet been effected, the derivatives of these electromers have been obtained and their chemical properties explained and correlated in terms of their electronic formulæ In other words, *the simultaneously formed ortho-, meta-, and para-substituted derivatives of a given compound are the immediate and direct reaction products of the electromers of that compound*

(5) The electronic conception of positive and negative valence, as herewith presented, developed and applied, is a formulative hypothesis Such an hypothesis to be efficient must be *inductively true* at the time of its promulgation, that is, it should explain the phenomena and laws which classification has brought together in a particular branch of science It should also be applicable to future discoveries, and, finally, it must be *deductively suggestive* in indicating lines of future research The electronic conception of positive and negative valence has, in a measure, met the first requirement in affording interpretations of the mechanism of many hitherto unexplained chemical reactions,

notably substitution reactions in the benzene nucleus and the anomalous behaviour of many derivatives of benzene It has also afforded explanations of physico-chemical phenomena such as molecular volume relationships, absorption of light and fluorescence Does it also meet the other fundamental requirement of a good hypothesis, namely, to suggest lines of future research?

B. Suggested Lines of Future Research.

A suggested line of research may be found in endeavours to isolate electromers, the existence of which in tautomeric equilibrium is clearly substantiated As noted, electromers of derivatives of benzene have not as yet been individually isolated, but a well-established case of electromerism has been pointed out by Jones (loc cit) in his electronic explanation of certain isomeric derivatives of hydroxylamine originally prepared by Meisenheimer These represent the first known instances of independently existing electromers, that is, compounds completely identical in structural formulæ but differing in physical and chemical properties by virtue solely of a different arrangement of the respective positive and negative valences (valence electrons) of certain constituent atoms The isolation of other electromers depends upon future research.

Another line of suggested research may be located in the well-ploughed field of unsuccessful attempts to effect a direct asymmetric synthesis, i e, to prepare a compound which displays optical activity through rotation of the plane of polarized light by virtue of its containing an asymmetric atom, e.g, the carbon atom, united to four chemically different atoms or radicals A suggestion to this end may exist in the following explanation of magnetic optical activity in terms of the electronic conception of positive and negative valence.

A naturally optically active carbon compound is either dextro- or lævo-rotatory *independently of the direction* in which the plane polarized light passes through its solution. On the other hand, a magnetically optically active liquid is dextro- or lævo-rotatory *according to the direction* in which the light passes through it, the magnetic field being constant. Now natural optical activity of a carbon compound depends upon the presence of an asymmetric carbon atom in its molecule. Briefly illustrated (C a, b, c, d) indicates that the quadrivalent carbon atom is united to four chemically different atoms or radicals, *a*, *b*, *c*, and *d* The compound (C *a*, *b*, *c*, *c*) is not optically active since two of the four atoms united to it (*c* and *c*) are chemically identical. But (C *a*, *b*, *c*, *c*) displays optical activity in a magnetic field. One natural conclusion is that the two chemically identical atoms (*c* and *c*) must function differently in the magnetic field In other words, in terms of the electronic conception, whether (*c*) and (*c*) are naturally both positive or naturally both negative, *the magnetic field induces a rearrangement of the valence electrons in such a way that one* (*c*) *functions positively and the other* (*c*) *functions negatively* It has been shown that a given atom may function sometimes negatively, sometimes positively, and these two states are entirely different chemically Hence, the magnetic field may induce magnetic optical activity by converting inactive $(\mathrm{C}\, a, b, \overset{+}{c}, \overset{+}{c})$ or inactive $(\mathrm{C}\, a, b, \overset{-}{c}, \overset{-}{c})$ into magnetically optically active $(\mathrm{C}\, a, b, \overset{+}{c}, \overset{-}{c})$ This may be termed *electromeric asymmetry*, the occasion of magnetic optical activity

It is also quite conceivable that a compound such as $(\mathrm{C}\, a, b, \overset{+}{c}, \overset{-}{c})$ in which like atoms (*c* and *c*) possess opposite polarity would not show optical activity unless in a magnetic field In this case the magnetic field would not be the occasion of atoms (*c* and *c*) functioning positively and negatively, but it would differentiate them in their relative spatial positions in the molecule so that the carbon atom (C) is asymmetric It displays electromeric asymmetry This differentiation in space and in polarity of the atoms ($\overset{+}{c}$ and $\overset{-}{c}$) in a magnetic field is readily correlated with the fact that a magnetically optically active liquid is dextro- or lævo-rotatory according to the direction in which the light passes through it

This proposed hypothesis also correlates the well-established theory of the asymmetric carbon atom of Le Bel and Van't Hoff with Faraday's discovery of and Sir W H Perkin's remarkable researches in the field of magnetic optical activity

Immediately in this connection it should also be noted that many crystalline substances, such as quartz, are optically active, but it has been held by physical chemists that the activity here is not due to the arrangement of atoms within the molecule but rather to a certain undefined arrangement of crystalline particles.

Now X-ray and crystal structure investigations are clearly indicating the types of the arrangements of the atoms in spaced lattices Accordingly, it is quite possible that many such arrangements present examples of *electromeric asymmetry* In other words, optical activity of crystals is assumed to be due to electromeric asymmetry which exists naturally in optically active crystals but is induced in inactive substances by the magnetic field

The suggestion of the conception "electromeric asymmetry" does not, of course, in itself constitute an explanation, but it may serve as a nucleus for the development of a more comprehensive hypothesis which should embrace and correlate, along the lines indicated, all types of optical activity The underlying concepts are the electronic conception of positive and negative valence and the principle of asymmetry, which latter has played a vital part in the explanation of the optical activity of compounds of carbon.

The phenomena of magnetic optical activity and the proposed electronic interpretation also suggest other lines of investigation For example, may not a sufficiently powerful magnetic field have some effect upon the relative concentrations or relative reactivities of the electromers in a tautomeric equilibrium mixture such as $(\overset{+}{C_6H_5}\ \overset{-}{X} \rightleftharpoons \overset{-}{C_6H_5}\ \overset{+}{X})$? Since benzene derivatives display electronic tautomerism, they may be expected to react differently within a magnetic field than they do in a non-magnetic field. This difference in reactivity under the two conditions could be ascertained by a quantitative determination of the reaction products which are the derivatives of the respective electromers. If the magnetic field altered in any way the concentrations or reactivities of the electromers, $\overset{+}{C_6H_5} . \overset{-}{X}$ and $\overset{-}{C_6H_5} . \overset{+}{X}$, variations in the quantities of the substituted derivatives of $\overset{+}{C_6H_5} . \overset{-}{X}$ and $\overset{-}{C_6H_5} . \overset{+}{X}$ would establish the fact.

In this connection studies of the hydrolytic reactions of optically active and inactive compounds, within and without the magnetic field, are suggested. Also, addition reactions present subjects for investigation. For example, the addition of the halogens and halogen acids to unsaturated compounds have a special significance in attempts to effect asymmetric synthesis.

The two types of double bonds, *contraplex* and *diplex*, proposed by the author afford a ready explanation of the varied and apparently anomalous addition reactions frequently noted in the literature How will a magnetic field effect these addition reactions?

The variable physical conditions under which these suggested reactions may be conducted must not be overlooked Electronic tautomers are undoubtedly very subtle. The behaviour of electromers and the possibility of their isolation are quite likely to be influenced by the magnetic field, its character and intensity, by the solvent medium, its density, molecular volume, temperature, dielectric constant, chemical properties, etc , and by the presence of catalysts, either directly employed or as secondary products of the reaction. All of these conditions as well as the quantities of the reacting substances, and the quantities of the products of the reactions must be accurately standardized and carefully determined in any of the suggested researches

From the foregoing it is quite apparent that the electronic conception of positive and negative valence meets the two fundamental requirements of an efficient formulative hypothesis it not only explains many facts and phenomena—its first function —but it is also deductively suggestive in that it has indicated various lines of future research These hypotheses are proposed with the understanding that assumption is not necessarily presumption

Finally, a statement made in the introductory chapter will now bear repetition "In view of the fact that electronic formulæ, in many instances, have proven to be more precise and more significant than the customary structural formulæ in the explanation of chemical and physico-chemical phenomena and the mechanism of reactions, it is quite conceivable that the electronic conception of positive and negative valence as a formulative hypothesis may become a necessary adjunct to the structure theory This, of course, must depend upon the nature and extent of its applications and experimental verifications, and upon the part that should be played by just criticisms in bringing to light the relative merits and demerits of its applications" Complementary to this opinion the author begs to conclude this monograph by quoting the final paragraph of A W Stewart's *Recent Advances in Organic Chemistry* (loc cit.) —

"It is not to be expected that success will be attained at stroke. Much more probably, there will be a good deal fumbling and recasting to be gone through, just as there w before our present-day formulæ emerged from the melting-po Any suggestions, therefore, which tend towards the enlargeme of our ideas of chemical constitution should be welcomed b those who have sufficient critical spirit to grasp the failure of o contemporary formulæ under the strain of modern investigations

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